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THE PROBLEM OF VERTICAL ZONING

CHARLES F. PARK, JR.

ABSTRACT

The validity of the concept of vertical zoning in ore deposits has recently been questioned. A few of the many mines that show pronounced composition changes in a vertical plane are described. It is concluded that vertical zoning is a common field phenomenon.

ZONING in the horizontal is a generally recognized concept in ore deposits, but zoning in the vertical is frequently thought to be theoretical and is said to be absent in the field. This point of view was stated by Noble in his recent paper on the classification of ore deposits (13). Noble said: " . . . in its bearing on the classification of ore deposits, . . . the depth-zone classification more readily explains vertical zoning than lateral zoning, whereas in fact lateral zoning is fairly common but well-defined vertical zoning is exceedingly rare, almost nonexistent." The presence or absence of vertical zoning is a matter of field observation, though horizontal zoning would of necessity seem to imply vertical zoning. The purpose of this paper is to call attention to a few of the many field examples of vertical zoning.

Zoning in ore deposits may be divided into three intergradational classes, according to scale. They are: (1) Regional zoning, exemplified by the Southern Piedmont region or by the mineral deposits associated with the Sierra Nevada batholith (14); (2) District zoning, which includes the well known mining districts of Butte, Montana (20), Cornwall, England (5, 11), and Bingham, Utah (15); and (3) Orebody zoning as defined by Riley (19). Regional zoning is on such a broad scale that individual mines or mining districts cannot possibly demonstrate the concept. Actually little is known of regional zoning, and it is not considered here. In zoned districts a few mines are "strategically" located where mineralization of one zone passes into that of another. Examples of mines in zoned districts and from zoned ore bodies are described below.

Vertical zoning is, at least in part, a function of the rate of temperature-pressure change, as pointed out by Stôçes (25), by Graton (9), and by Borchert (2). At great depths changes in temperature and pressure take place slowly and through considerable distances. Here zones are widely spaced and transitions between them are generally gradational through large distances. For this reason deep mines of hypothermal types seldom show vertical zoning. An exception to this generalization is the Kolar Gold Field, where the fineness of the gold systematically increases from 800 in the upper levels to 930 at depth (17). Toward the surface of the earth, temperatures and pressures of an ascending fluid would be reduced more rapidly than in depth; zones are therefore more closely spaced near the surface and are brought within the scope of ordinary mine operations.

Zoning in epigenetic ore deposits usually refers to concentrically arranged layers that contain different minerals—ores, alteration products, and gangue minerals. Zoning is best developed where deposition of ore was largely independent of the nature of the enclosing rocks. Thus bedded replacement deposits in limestones and other rocks ordinarily would show no well-defined zoning. Likewise, where wall rocks have markedly influenced deposition, vein-type deposits probably would not be zoned. Excluded also would be certain ore shoots where structure and obscure features have strongly influenced localization. Conversely, zoning would be best where mineralization took place during one continuous period. Should the introduction be in several surges or at widely separated times, zoning might not be recognized.

Most epigenetic ore deposits in the epithermal and mesothermal zones that extend through considerable vertical range, change character at depth. Many deposits simply pinch out. In others, the character of the mineralization changes with depth. Gold-silver bonanzas, such as those of the Comstock Lode, Nevada (8), of Mogollon, New Mexico, of Chañarcillo, Chile, and of a host of others, were sunk in primary mineralization to their economic limits. At Mogollon, the Fanny mine bottomed at about 1,300 feet, but the vein persists to greater depths, unchanged except for a decrease in silver values. At the Azurite mine in the Cascade Mountains, Washington, the upper levels contained excellent gold values that gradually decreased with depth. The strong quartz-pyrrhotite vein persists below the deepest workings, but without appreciable gold. In central Chile many small mines have been opened on strong apatite veins, which in depth grade into apatite-bearing magnetite. These changes are as much phenomena of zoning as is the change from a lead-zinc vein to a copper vein at depth. Is not also an explanation of why mercury mines are shallow to be found in vertical zoning?

Excellent examples of vertical zoning were recognized by Kato (10) in the volcanic rocks of Japan. In the Daira mine, Ugo, veins are in Tertiary tuffs and andesite. The upper levels were worked for silver-lead-zinc, which gradually changes in depth to chalcopyrite-pyrite. Kato said: "The depth difference in ore minerals is very conspicuous." In the Takata mine, Rikuzen, the veins are in Tertiary tuff and propylitized andesite. The upper levels are in silver-bearing galena that changes in depth to sphalerite. Concerning these deposits Kato said: "The zonal distribution according to depth . . . is very pronounced."

A different type of deposit at the Washinosu mine, Rikuchu, was described, also by Kato. At the summit of Mount Washinosu a stockwork of intricately netted veinlets of gold-quartz ore gradually changes in depth to chalcopyrite and the network of veinlets converges to a few large veins. Kato also described the Nishizawa mine in Shimotsuke, and the Ogôto district in Echigo, where gold-silver-quartz veins change to tin-tungsten at depth. Kato concluded that the zonal arrangement of ores according to depth can be recognized in Japan in veins genetically related to late Tertiary volcanic activity.

Another excellent example of changes in vein composition in depth is the Red Mountain district, Colorado, described by Ransome (18) and later by Burbank (3). Ransome said: "One of the . . . facts in connection with the Guston, as well as with other mines in this district is the change in character of the ores with depth. The galena ore of the main ore body, carrying from 50 to 60 percent of lead and from 30 to 40 ounces of silver, continued down to the second level, or a little beyond, where it is said to have changed rather abruptly to a high-grade stromeyerite. Galena, however, occurred in the mine in considerable quantity down to the fifth level, 288 feet in depth, and in decreasing amounts to greater depths. . . . With increasing depth stromeyerite . . . became the characteristically rich ore of the mine, associated with pyrite and chalcopyrite. . . . Below the slip plane, . . . just below the seventh level, at about 500 feet in depth, the ore was harder and more compact and stromeyerite was not found in any quantity, the ore down to the tenth level consisting chiefly of large masses of low grade pyrite, with some bornite and chalcopyrite. In both the ninth and tenth levels there were small quantities of ore carrying free gold, assays from 9 level giving as much as 29 ounces of gold per ton." Similar descriptions of the Yankee Girl and other mines in the district convincingly demonstrate vertical changes in the hypogene mineralization.

Stickney, in describing the pyritic copper deposits of Kyshtim, Russia (24), said: "The important facts . . . are: (a) a gradual and regular decrease in the average width of the orebody with depth, and (b) a decrease in pyrite accompanied by an increase of gold, silver, quartz and aluminous material with increasing depth, while an increase in barite and zinc also appears to be indicated. In other words, a progressive decrease in width and change in relative composition of the ore with depth on a vertical section, similar in general to the variation occurring in the horizontal plane from the middle of the orebody outward, is at least strongly suggested." This mine was 970 feet deep at the time of the description.

Good examples of vertical zoning are recognized in Mexico. Simons and Mapes (22) describe the Carrizal mining area of Zimapan, where pyrometasomatic deposits grade both above and away from intrusive bodies into deposits of mesothermal zone type. Anderson (1) points out that in the Orito ore body in the Asientos-Tepezala district, Aguascalientes, quartz increases in depth, but calcite is more abundant toward the surface.

Schneiderhöhn (21) recognizes three vertical zones in the deposits at Joachimstal in the Sudetenland. Silver ores in the upper levels give way to complex cobalt-nickel-arsenic-bismuth ores in the middle levels. These in turn give way to uranium ores at depth.

At Oruro, Bolivia, Chace (4) found: " . . . observations made during the mapping of vein structure . . . and a study of assay records and of a suite of specimens . . . indicate . . . a considerable variation in the lateral and vertical distribution of metals and mineral types, not only in individual veins, but also in the district as a whole."

Forgan (7) described composition changes with depth at the Trepça mine, Yugoslavia. At depth lead stays almost constant, zinc and rhodochrosite decrease markedly, and silver, bismuth, and quartz increase. In the upper levels pyrite and pyrrhotite are present in about equal amounts, but at depth pyrrhotite increases.

Vertical zoning at Butte and at Cornwall are so well known that they hardly need to be mentioned—a few examples from Cornwall will suffice here. Lilley (11) stated: "Some zinc was found close to the surface in Old Dolcoath but the main value down to a depth of 1140 feet was . . . copper. . . . From that level to the bottom, the mine operated almost entirely for the tin. At the Tresavean mine . . . the copper zone was somewhat thicker, approximately 2070 ft. being passed through before the tin zone was reached . . . the full thickness of the lead-silver zone is in the now abandoned Wheal Mary Ann mine near Liskeard, where after passing through some barren ground the mine was carried to a depth of 1800 feet in workable silver-lead ore. Mining was stopped when copper began to appear. . . ." Davison (5) also confirms vertical zoning at Cornwall. Three shafts in the north of Camborne-Redruth mining area are the Roskear, 2,000 feet deep, East Pool and Agar, 1,400 feet deep, and the Tolgus, 2,000 feet deep. Each of these shafts cuts a sequence of veins and "in each case the veins cut near the surface carry galena, zincblende, and pyrite, with fluorite, siderite or ankerite, and quartz. Lower veins carry zincblende and pyrite with no galena but much chlorite; at still deeper levels copper minerals such as chalcopyrite and bornite occur with pyrite and zincblende, the chief gangue minerals being fluorite and chlorite. In the lower veins there is a small proportion of cassiterite but it was not until the shafts began to cut granite or approached the granite contact that the veins showed any considerable proportion of cassiterite."

Many other examples of vertical zoning might be cited. Lindgren (12) described the Leadville vein at Bingham, Utah, and stated that at a depth of about 2,000 feet it "changed from a low temperature lead-zinc vein to a tennantite-chalcopyrite ore." A similar change was described by Perry (16) at the Duluth pipe in Cananea, Mexico, where sphalerite-galena ore in the upper levels grades into chalcopyrite in depth. Lindgren (12) also stated that many lead veins change at slight depth into poor sphalerite-siderite-pyrite ores. Sjögren (23) in discussing the Bersbo mine, Åtvidaberg, said: "A striking feature . . . is the downward increase of zincblende with proportional decrease in copper." Finlayson (6) stressed the fact that in the lead-zinc veins of Great Britain galena and fluorite in the upper levels gave way to sphalerite and chalcopyrite at depth.

These examples amply demonstrate that vertical zoning is an observed fact, if by vertical zoning in epigenetic ore deposits is meant the usual concept of change of mineral composition away from a magmatic source. Gangue

minerals and alteration products are as much a part of vertical zoning as are the metallic constituents, and they must be included in any study of zoning. When this is done, vertical zoning is found to be a common field phenomenon.

In the preparation of this discussion, suggestions made by Adolph Knopf, F. L. Humphrey, and K. B. Krauskopf have been most helpful. Their assistance is appreciated.

STANFORD UNIVERSITY,
STANFORD, CALIFORNIA,
Feb. 20, 1957

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GEOCHEMICAL AND MINERALOGICAL INVESTIGATIONS OF TITANIFEROUS IRON ORES, WEST COAST OF NORWAY

TORE GJELSVIK

ABSTRACT

Geological setting, mineralogical and petrographic descriptions are given for 4 titaniferous iron ore deposits, most of which have been subjected to regional metamorphism strong enough to extinguish primary features. Chemical analyses of major and minor elements of the ores and the oxide minerals have been carried out, and the data discussed in relation to the genetic problems.

Definite conclusion is reached for one occurrence only, which is an ore rich ferrogabbro of late intermediate crystallization. Most of the geochemical factors support the theory of magmatic formation of the other deposits, but discrepancies exist, and formation by metasomatism, at least of one type, cannot be ruled out.

If the theory of magmatic origin is right, the metamorphic effects upon the elements of the Fe-Ti-oxides have been: rapid removal of Ti from magnetite, while Fe^3 (in form of hematite) in ilmenite is stable. Also Mg in magnetite, and Mg and Mn in ilmenite, and most of the trace elements in both oxides, seem fairly stable.

INTRODUCTION

MANY titaniferous iron ores are found in the fjord areas of western Norway. A few of them have been mined; at the present time only two are exploited. The deposits occur in four districts. In the extreme south-west they occur within the great anorthosite province of Egersund-Sogndal, partly as ilmenonorite dikes (e.g., Storgangen, the largest titanium mine in Europe), and partly as schlieren or lenses of high-grade ilmenite ore (Blåfjell type). The Egersund-Sogndal rocks occur within the large Precambrian gneiss area of Southern Norway. The rocks and their ore deposits have been described in a number of papers, especially those of J. H. L. Vogt (12) and C. F. Kolderup (7).

The second district is the Bergen area, in which small lenses of titaniferous iron ore occur partly within anorthositic rocks and partly within gabbros and amphibolites. The occurrences have not been treated in detail; references are made to Vogt (13) and Kolderup, C. F. and N. H. (8).

A group of titaniferous iron ores occur in the Sunnfjord district, north of Sognefjord (Vogt 13). The host rocks are metamorphosed gabbroic rocks or chlorite schists.

The district investigated by the author is the Sunnmøre gneiss area, in which titaniferous iron ores are distributed in a broad belt, continuing northeasterly into Romsdal and Nordmøre. The Rødsand mine in Nordmøre has been in operation for a long time. Recently, the Solnør-Sjøholt deposit in Sunnmøre has been extensively investigated and has proved to contain several

million tons of ore. In the previous literature all the Sunnmøre and Romsdal titaniferous iron ores have been classified in a single group, named the Rødsand type, and they have been thought to be genetically related.

During the reconnaissance studies of this district the author found that the ores consisted of at least 2, probably 3 different types (3). More detailed studies revealed that the Rødsand "type" consists of so many different types that this classification is untenable. Each deposit shows individual characteristics in geologic, mineralogic, and chemical relationships. The aim of the present study is purely scientific, but it was thought that a careful mineralogical and geochemical investigation would be of importance for the metallurgical treatment of these ores. None of the deposits of the present investigation seem very promising from an economic viewpoint, mainly because they are small.

GENERAL GEOLOGY OF THE AREA

A description of the geological formations was published by the author in 1951 (3), and in 1953 another paper (5), dealing with the age relationships and stratigraphic-tectonical setting of the gneisses, was published. Most of the rocks are granodioritic gneisses, including metasediments, quartzites, schists marble, and numerous, but small lenses of a variety of mono-mineralic or ultramafic rocks (anorthosite, dunite, amphibolite and eclogite). Narrow bands of greenschists, probably metabasalts, occur in some places. The northern part of Sunnmøre, Romsdal and Nordmøre contains a great number of dolerite lenses (4), which is one of the few rocks within the gneiss area that clearly exhibits primary, magmatic features. The metamorphic facies show no great variation within the area. Most of the gneisses belong to the amphibolite facies; to the east they may be a little lower (epidote-amphibolite facies), and westward, granulite facies conditions are approached. The gneisses are strongly folded; isoclinal structures have been disclosed in some places. The southern part is more gently folded. The orogenic history of the area includes a late phase of intense granitization, which makes it difficult to obtain a clear picture of the early stages of rock formation.

The area was considered formerly to be the western Precambrian foreland of the Caledonian range in Norway. Most authors now agree that it belongs to the central part of the Caledonian orogeny, and that Precambrian basement rocks have been thoroughly altered, mineralogically and structurally, during that period.

EARLIER WORK ON THE TITANIFEROUS IRON ORES

Only the Rødsand ore has been described in detail by previous authors. Of most interest is Vogt's paper (14) which gives a geological description, as well as mineralogical and chemical data concerning the ore. According to him, the ore occurs in lenses within bodies of "gabbro schists," which again are inclusions in a wide and long zone of "sheared granite," a term that probably corresponds to granitic gneiss. Vogt thought that the rocks were genetically related, forming a differentiation series of a granitic magma. No special evidence, however, was given. Mineralogically, the Rødsand deposit is of

interest since it contains corundum as an accessory. Commonly, spinel is the Al-bearing oxide in the titaniferous iron ores.

In the Sunnmøre dolerite series, Fe-Ti oxides are common constituents and may be present in considerable amounts (4). The oxide minerals are of the same kind, and exhibit the same textural relationship as the ore minerals in the only commercial deposit so far found within these dolerites (Solnør-Sjøholt). The contact between the orebodies and the dolerite mother rock may be sharp or gradual (4, p. 96–97).

Since the above paper was written, the author has investigated a number of titaniferous iron ores in Sunnmøre. In this paper, however, only 4 are treated in detail.

DESCRIPTION OF DEPOSITS

Fiskå, Vanylven

At Fiskå, the ore is found within an anorthosite of somewhat larger size than most of the anorthosites in this gneiss area. It is largely covered by peat and soil, much of it is under the sea. The width of the anorthosite is half a mile and the length on the land side is approximately 2 miles. The anorthosite is locally very coarse-grained having individual crystals six inches across. These giant crystals contain 45–50 percent An, and they commonly exhibit good crystal faces. Interstitally, hypersthene (En_{70-75}) is found in small amounts but commonly in large crystals and in all cases with coronas of amphibole and garnet. The iron oxides also occur in the interstices, generally together with hypersthene, surrounded by coronas of sphene and garnet, or also of biotite, hornblende, and plagioclase.

Shearing, causing granulation, has greatly affected the coarse-grained anorthosite. Along the margins of the lens, a schistose, sugary, and foliated rock has been formed, which may be difficult to distinguish from a light-colored gneiss. The minerals are andesine (slightly more sodic than the giant crystals), mica, amphibole, epidote-zoisite, chlorite, and quartz. Accessories are iron oxides, rutile, sphene, apatite, and scapolite. In the central part of the lens, the giant crystals were broken down, and a cataclastic texture formed. Secondary minerals were formed only to a moderate extent, except for some shear zones, in which were developed the same minerals and structures as in the contact zones.

Titaniferous iron ore occurs in two different ways: as irregular segregations in the coarse-grained, central part of the anorthosite, and in "cross-cutting" dikes of noritic to gabbroic composition, also in the axial part of the anorthosite lens. The segregations generally are of the same size as the giant feldspar crystals, and large hypersthene (En_{77}) crystals may be found in them, too. Even where most abundant, the segregations do not constitute more than 10 percent of the rock. The noritic dikes are small, generally less than 1 m wide and a maximum of 5 m. They are found only on a little island and their length is unknown. They have been subjected to the same shearing as the anorthosite, but are even more altered. The primary minerals are plagioclase (present composition An_{20-30}), hypersthene (En_{55-60}), Fe-Ti oxides, and

augite (rather subordinate or lacking in thin-sections). The amount of oxides present also varies. In some dikes, apatite, in idiomorphic crystals, is rather abundant. Secondary minerals are: garnet (mostly of the almandine component), hornblende, anthophyllite(?), biotite, quartz, and hematite. Garnet occurs partly as small corona crystals (Fig. 1), partly as rounded, subidiomorphic crystals of the same size as the primary silicates, and in some dikes it constitutes around 50 percent of the rock.

Ore Minerals.—In the segregations, ilmenite exceeds magnetite, and invariably contains tiny, oriented lamellae of hematite (Fig. 2). Magnetite forms individual grains, but in some places there is a remarkable parallel orientation of tabular magnetite crystals in ilmenite. In one specimen, magnetite is selectively replaced by hematite, partly along certain crystal faces,

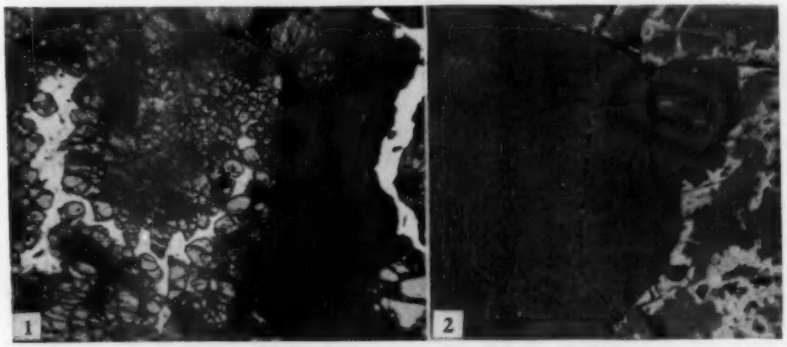

FIG. 1. Thin section of M 1044, ilmeno-noritic dike, Fiskå. Garnet corona of ore minerals. Interstitial character of ore minerals towards hypersthene, (abundant cleavage cracks). × 22.

FIG. 2. Polished section of M 852, ore segregation in anorthosite, Fiskå. Illmenite with hematite, inclusions (left). Martitizel magnetite (right). × 150.

partly along grain contacts, or in veins (Fig. 2). Furthermore goethite is formed, mostly in veins that cut ilmenite. Spinel, a major constituent of the oxide fraction, forms individual crystals, heavily clouded by tiny crystals of magnetite and ilmenite. Between ore minerals and spinel a brown, pleochroic mineral has formed, it is similar to høgbomite, but it has not been identified positively.

In the noritic dikes, ilmenite, with the same hematite intergrowth as described above, is in even greater predominance in relation to magnetite than in the segregations. Only a few grains of magnetite are visible in polished sections, and spinel (clear green) occurs only as inclusions in magnetite. The Fe-Ti ore crystals are always interstitial towards the primary silicates, and may even replace apatite and to a slight extent also pyroxene. The oxides also tend to concentrate in veinlike bands within the dikes. On the other hand, the ore minerals are surrounded by reaction zones, mainly of garnet and biotite (Fig. 1), thus they formed before the main regional metamorphic period.

Verkshaugen, Bergsøya

In this place the ore occurs in the central part of an eclogite lense, approximately 1 mile long, and a few hundred m wide. The surrounding rocks are mainly garnet-hornblende-biotite-gneisses containing a great number of eclogite inclusions. Gneissic anorthosites also occur in the area.

Near the ore, the eclogite, which is medium-grained, consists of garnet (with a corona of hornblende), and a symplectite of diopside and plagioclase (pseudomorphic after omphacite), and some interstitial iron ore that looks rather resorbed. The original omphacite is found as relics in a few of the symplectites. The greatest part of the lens is made up of coarser grained eclogite-amphibolite, which is even more altered by retrograde metamorphism than the other type.

In the central part of the lens, a conspicuously banded rock has developed. The bands are mostly about 1 dm wide and rarely as much as 1 m. Some bands are almost garnetfels, with small amounts of hornblende and diopside, whereas others consist of olivine, Fe-Ti oxides, bronzite, and garnet. These are the extremes, other bands may contain different proportions of all of these minerals. A few bands, strongly sheared, contain mostly hornblende and chlorite. The texture of the ore-rich bands is shown in Figure 3. Olivine (Fo_{85}), slightly serpentinized, forms subidiomorphic crystals, garnet (pyrope rich) forms mostly rounded or sausage formed crystals, and it is always surrounded by a wide corona of a fibrous mineral probably hornblende, but too thin to be identified. The Fe-Ti ores and rhombic pyroxene (En_{90}) partly form individual crystals, interstitial to olivine, partly tiny ore crystals form form individual crystals, interstitual to olivine, partly tiny ore crystals form wormlike intergrowth in rhombic pyroxene, something like a myrmekite pattern (Fig. 4). The aggregate is mostly found along the contact of olivine crystals, but in places between olivine and iron ore. In some places it looks as if it is formed at the expense of olivine, but it is not like an ordinary corona.

Ore Minerals.—The oxide fraction consists of magnetite, ilmeno-hematite, and small crystals of clear, green spinel (Mg-rich). Besides forming intergrowths with enstatite, magnetite also forms individual crystals, generally with narrow, oriented spinel lamellae, but without ilmenite lamellae. Ilmenite and hematite form the same intergrowths as those in the Fiskå ores. The amount and the size of exsolved hematite seem to vary greatly in different grains.

Øyen, Tafjord

The rock surrounding the ore body in this area, is a schistose and fine-grained, plagioclase-rich gneiss containing some biotite, hornblende and garnet. Quartz and microcline are subordinate to plagioclase (An_{35-40}), and seem to replace it. In some parts, wholesale replacement of hornblende by epidote and chlorite has occurred; biotite and garnet are replaced only by chlorite. Small veins of epidote and chlorite, or also of sphene, intersect the gneiss in many places. In the gneiss, the ore-body forms a flat, concordant lense.

The ore itself is rather heterogeneous. The most common type consists of garnet (Fe-rich) and Ti-Fe oxides, with some plagioclase (oligoclase to

andesine, commonly poikilitic), and a little biotite. In other parts, a green hornblende is abundant. Epidote and apatite are accessories. In one section, the Fe-Ti oxides occur in the base of a mineral, whose optical properties in-

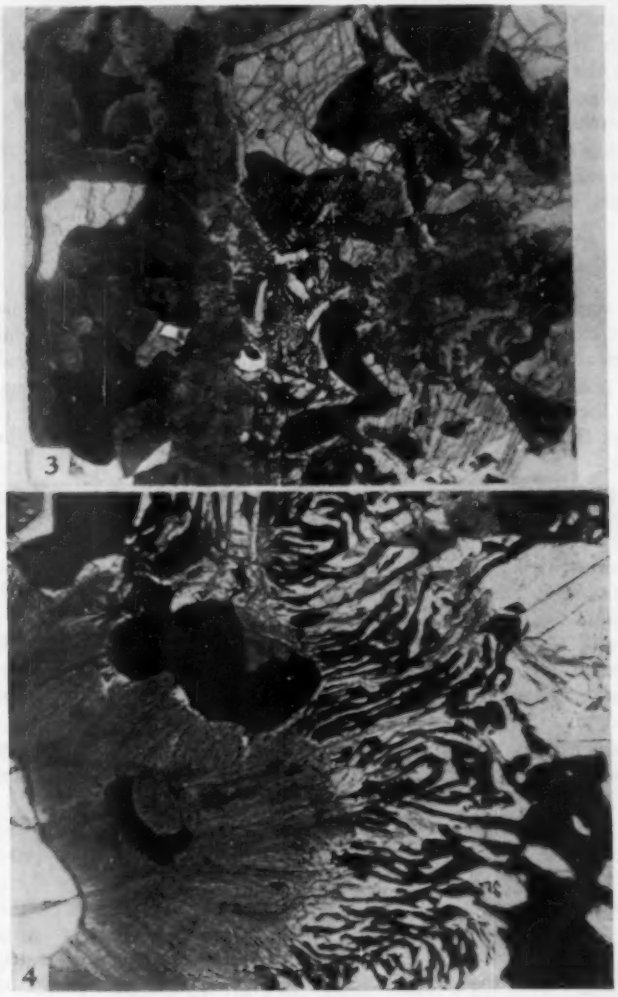

FIG. 3. Thin section of M 868, ore rich band in eclogite, Verkshaugen. Left: garnet with corona. Right: enstatite, and magnetite-enstatite symplectite.

FIG. 4. As in Figure 3, but larger magnification. Details of garnet corona and magnetite-enstatite symplectite. In upper part of the latter, also some spinel (half opaque). × 180.

dicate cordierite, but it does not exhibit any pseudohexagonal twins. The ore, furthermore, is replaced or intersected by veins of chlorite and sphene.

Ore Minerals.—Magnetite is more abundant than ilmenite, and forms larger, idiomorphic crystals, some with lamellae of spinel. Ilmenite in some places exhibits beautiful, polysynthetic twins. In some grains hematite exsolution discs are clearly visible under the microscope, in others they can be seen only by the greatest magnification. Also ilmenite has a tendency to form idiomorphic crystals. In rare cases, magnetite and ilmenite form lamellar intergrowths.

In some parts of the Øyen ore, sulfides, mostly pyrite and chalcopyrite, are more abundant than usual in these oxide ores. They generally occur in veins or patches, and seem to belong to a younger generation than the oxides.

Øvre Røddal, Tafjord

In a narrow valley, separated from the Øyen occurrence by a high, steep ridge, an extremely iron-rich gabbro occurs within a leucogneiss, which may have been an anorthosite but now the feldspar is mostly perthite with abundant relics of plagioclase. Only small amounts of quartz are present. The contact between the gneiss and the gabbro is not sufficiently exposed to give a clear picture of the relationship, but it is most probably conformable to the gneiss structure.

The primary minerals of the gabbro are: plagioclase, olivine (Fo_{28}) (surprisingly fresh), augite (subordinate), and iron oxides and apatite in quite varying proportions. Høgbomite is an accessory. Perthite occurs as a clearly secondary mineral replacing plagioclase to such an extent as to make the determination of the latter by optical properties, impossible. Furthermore garnet (almandine) also replaces plagioclase along cleavage directions. Granular crystals of clear green diopside in rare cases replace olivine. Biotite is probably secondary because it generally has been formed near iron ores. In a few cracks, serpentine, chlorite, and iron ore are formed. The texture of the rock is eugranitic (gabbroic).

In some places, the iron ores (and olivine) have been strongly concentrated. The exposures are not good enough to disclose the pattern of the concentrations. Contacts seem to be rather gradual, however.

Ore Minerals.—In the ore-rich parts, ilmenite greatly exceeds magnetite. The contacts between them are clean, and no lamellar intergrowths can be seen. Polysynthetic twins of ilmenite are observed, but not even by the greatest magnifications can exsolution blebs of hematite be seen. Besides the ilmenite lamellae, magnetite contains a very fine, oriented network of another oxide mineral, which is similar to ilmenite, but the pattern is more like magnetite-ulvøspinel intergrowths (Fig. 5). Furthermore, the analysis of the magnetite does suggest that the enclosed minerals are ulvøspinel. X-ray investigations, however, failed to disclose any ulvøspinel.

Another mineral, nearly opaque, is found clustered around the iron oxides. It is thought to be høgbomite.

The ore crystals fill the interstices between the silicates, and also form a sort of intergranular film (Fig. 6).

CHEMICAL DATA

Preparation of Material.—The bulk chemical analyses of the ores (Table 1) have been made on samples weighing between 0.5 and 1 kg. They do not

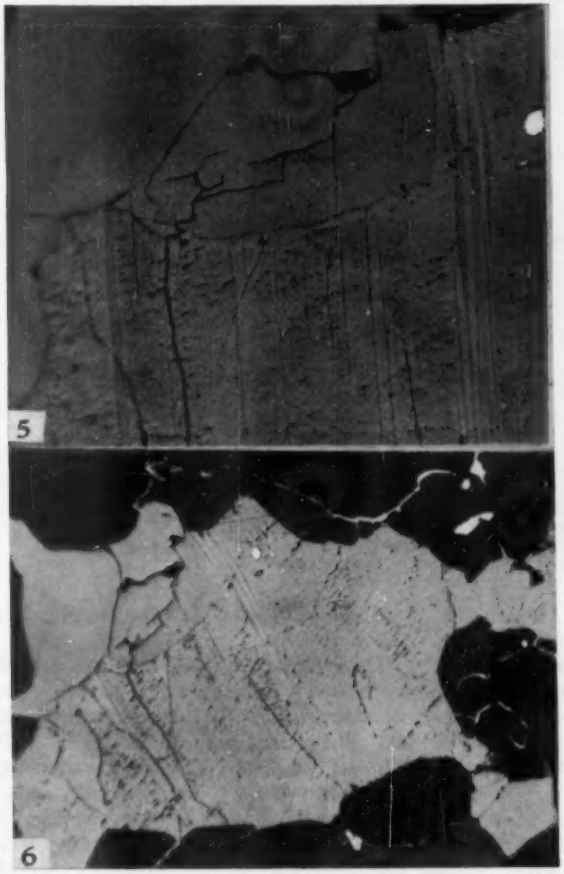

FIG. 5. Polished section of SM 1106, Øvre Røddal, Tafjord. Upper part: Ilmenite, with smooth, grey surface. Lower part: Magnetite, with vertical, parallel plates of ilmenite, and diagonal cross pattern, thought to represent intergrowth of ulvøspinel and magnetite. × 180.

FIG. 6. As Figure 5, but smaller magnification. Note thin, intergranular veins of ore between silicate crystals. × 85.

TABLE 1

ANALYSES OF FE-TI ORES AND RELATED ROCKS

W%	Fiskå, Vanylven		Verkshaugen		Øyen	TØ. Rødal		I	II	III	IV
	Segr.	M 1044	M 868	M 994	M 331	SM 1105	SM 1106				
SiO_2		29.09	24.59	42.47	22.45	35.16	25.27	21.84	44.95	22.35	31.59
TiO_2	16.4	15.98	5.60	3.54	7.97	5.13	6.16	5.04	1.73	10.11	18.49
Al_2O_3		9.27	7.43	17.00	11.80	9.18	5.39	7.65	19.35	5.26	8.54
Fe_2O_3	33.4	13.36	19.70	3.14	24.62	9.00	3.10	15.78	2.30	14.05	2.36
FeO	29.0	20.06	22.44	15.50	24.06	21.53	40.88	26.39	10.47	28.84	24.52
MnO	0.22	0.22	0.23	0.12	0.29	0.73	1.08	0.34	0.16	0.43	n.d.
MgO		6.24	18.50	7.23	3.22	4.24	7.12	18.93	7.52	16.10	10.70
CaO		3.66	1.16	9.50	2.46	6.97	6.29	0.73	7.82	1.17	2.25
Na_2O		1.16	0.00	1.55	0.80	2.24	0.55	0.28	2.80	0.44	1.03
K_2O		0.34	0.00	0.00	0.85	1.67	0.50	0.18	0.81	0.10	0.15
$H_2O^{-110°}$		0.12	0.08	0.04	0.08	0.37	0.08	2.30	0.04	n.d.	n.d.
$H_2O^{+110°}$		0.45	0.31	0.25	1.38	0.57	0.22		1.18	n.d.	n.d.
P_2O_5		0.20	0.00	0.05	0.05	3.24	4.19	0.12	0.31	0.02	0.02
CO_2		n.d.	0.00	n.d.	0.00	0.00	0.00	n.d.	n.d.	0.02	n.d.
Sum		100.15	100.04	100.39	100.03	100.03	100.11	99.84	99.61	99.15	99.65
F								0.02	0.06		
S								0.06	0.20	0.38	
Zn										0.71	
Ni										0.08	

Segr. Fiskå, average of M 852 and M 1046.
M 1044, ilmeno-noritic dike in anorthosite, Fiskå, Vanylven.
M 868, ore-rich band in central part of M 994.
M 994, eclogite lens, Verkshaugen Bergøya.
M 331, average ore type, Øyen Tafjord.
SM 1105, ferrogabbro, Øvre Rødal, Tafjord.
SM 1106, ore-rich ferrogabbro, Øvre Rødal, Tafjord.
I, Magnetite olivinite, Taberg, Sweden (Hjelmquist, 1950).
II, Hyperite, Taberg, Sweden (Hjelmquist, 1950).
III, Cumberlandite, Iron Mine Hill (Hjelmquist, 1950).
IV, Average ilmeno-norite ore, Storgangen, Sogndal (13).

represent "average ore" in an economic sense, but the samples were selected as typical of the ores and rocks in question.

After the first crushing, the material was split and one portion used for separation of magnetite and ilmenite. The separation, however, proved to be difficult because the rocks contained garnet and other heavy minerals, in reaction zones around the oxides. The grain size of the oxides range from 0.1 to 1 mm. The fraction 0.15–0.10 mm was used for the separation. Sometimes repeated crushing and sieving were necessary, but generally, fractions below 0.07 mm could not be used, owing to lack of an adequate centrifuge.

Magnetite was removed by hand magnet, then separated in Clerici solution (Sp. Gr. = 4.05), washed and dried, and repeatedly carried through a Franz isodynamic separator with the current off. The concentrate was then placed under a binocular microscope and iron chips (from the crushers) and silicates were picked out. By this procedure, most magnetite concentrates contained less than 3–4 percent impure grains, most of which were magnetite coated with garnet. One sample, M 1044, did not give a useable concentrate, and

another, M 868, as shown by its high SiO_2 value (Table 2), was not concentrated too successfully. In the latter case, the explanation may be the fine-grained symplectic intergrowth of magnetite and pyroxene (Fig. 4), and garnet.

From the residue after the hand magnet separation, ilmenite was removed by the Franz separator, then further concentrated by warm Clerici solution (sp. gr. > 4.05) in order to remove composite grains containing garnet, olivine, and spinel, all of which have specific gravities close to 4. The final purification was done in the same way as for magnetite. Most ilmenite concentrates were very pure, probably over 99 percent.

TABLE 2

CHEMICAL ANALYSES OF MAGNETITES AND ILMENITES

W%	Magnetites					Ilmenites					
	M 331	M 852	M 868	M 1046	SM 1106	M 331	M 852	M 868	M 1044	M 1046	SM 1106
SiO_2	0.9	0.1	3.6	0.2	n.d.	0.3	0.2	0.2	0.2	0.1	0.1
TiO_2	1.1	0.5	1.9	1.–	14.6	46.9	45.1	50.2	38.7	46.3	50.2
Fe_2O_3	63.4	71.8	57.4	64.8	44.1	8.9	18.4	7.3	29.2	12.8	2.5
V_2O_3	1.–	1.–	0.9	0.8	0.1	0.3	0.3	0.2	0.8	0.2	0.–
Cr_2O_3	1.9	0.3	0.1	0.1	0.–	0.1	0.–	0.–	0.1	0.–	0.–
FeO	31.3	26.1	31.4	32.–	41.5	41.6	33.1	35.1	30.1	38.9	46.5
MgO	n.d.	0.8	3.5	0.4	0.–	0.8	3.1	6.6	1.6	1.5	0.–
MnO	0.–	0.–	0.1	0.–	0.3	0.7	0.5	0.5	0.1	0.4	0.9
Sum	99.6	100.6	98.9	99.9	100.6	99.6	100.7	100.1	100.8	100.4	100.2
$FeTiO_3$					11.4	93.6	89.–	94.2	81.4	91.–	96.2
Fe_2TiO_4					35.4						
Fe_3O_4	94.8	90.6	86. -	94.–	53.2	3.8	9.5	4.8		2.–	2.4
Fe_2O_3	3.6	9.3				2.6	1.5	1.–	16.7	7.–	
TiO_2	1.6	0.7							1.9		
FeO			5.9	1.8							1.4

Index is given in Table 1. n.d. = not determined.
0.– means at least less than 0.05%.

The mineral concentrates thus obtained, were mostly too small for ordinary chemical analyses, and the micro-chemical methods described by Vincent and Phillips (11), were therefore used. The results of the mineral analyses are given in Table 2.

Not all of the mineral analyses are perfect, as shown by the totals, but the determinations were repeated for most of the elements, and the errors are probably of minor importance. The magnetite specimen M 868, with 98.9 percent iron was contaminated by silicates, and in addition to the elements determined, it may contain Al and probably some Ca.

In Table 2 the analyses also have been calculated to mol percent of ilmenite, magnetite, hematite, and ulvøspinel, as well as excess oxides. None of the samples consist of a "pure" mineral. Though some of the "impurities" may be the result of inadequate separation, most of it comes from minute exsolution bodies or from solid solutions. It is seen that where the magnetite in a rock is high in Fe^2, the ilmenite is low in Fe^3.

The samples used for spectrochemical analyses (Table 3), have been carefully cleaned under the binocular microscope, and thus were free of contamination by silicates.

TABLE 3

TRACE ELEMENTS OF ORES, MAGNETITES (MT) AND ILMENITES (I) FROM SUNNMØRE

	P.p.m.						Distribution ratios					
	Cr	Ni	Co	Cu	V	Mn	Cr	Ni	Co	Cu	V	Mn
M 331	3,900	280	160	100	2,500	2,400						
Mt 331	13,000	480	170	60	7,100	120	26	3.4	0.8	>1.5	3.9	1
I 331	500	140	210	<40	1,800	5,400	1	1	1	1	1	45
M 868	200	600	210	600	900	1,600						
Mt 868	700	1,200	300	60	6,200	720	7	3.7	1	>1.5	4.8	1
I 868	100	320	300	<40	1,300	3,600	1	1	1	1	1	5
M 852	1,100	400	220	400	2,100	1,600						
Mt 852	2,100	610	180	80	6,700	180	12	4.5	0.9	>2	3.1	1
I 852	180	140	210	<40	2,200	3,600	1	1	1	1	1	20
M 1046	1,400	220	210	120	2,000	1,600						
Mt 1046	4,700	220	150	60	5,700	100	26	>2.7	0.7	>1.5	3.8	1
I 1046	180	<80	210	<40	1,500	3,200	1	1	1	1	1	32
M 1044	200	<80	<75	65	1,200	1,600						
Mt 1044	2,100	130	120	220	4,800	500	4.7	>1.6	>1.6	>5.5	1	1
I 1044	450	<80	<75	<40	5,000	1,100	1	1	1	1	1	2.2
SM 1105	<35	<80	<75	50	300	5,700						
I 1105	<35	<80	<75	<40	<30	6,900						
SM 1106	<35	<80	<75	80	500	8,900						
Mt 1106	<35	<80	<75	240	600	2,100				3	>10	1
I 1106	<35	<80	<75	80	<60	7,200				1	1	2.9

M 331: average ore type, Øyen, Tafjord.
M 868: ore rich band, Verkshaugen, Bergsøya.
M 852 and M 1046: segregations in anorthosite, Fiskå, Vanylven.
M 1044: ilmeno-noritic dike in anorthosite, Fiskå, Vanylven.
SM 1105: ferrogabbro, and SM 1106 ore-rich ferrogabbro, Øvre Røddal, Tafjord.

Trace Element Distribution.—The chemical data of the ores and minerals will be discussed in the next section. Only a short comment on the trace element distribution is given here.

Generally, the geochemical figures of the Sunnmøre series are in good agreement with known data. Cr is strongly concentrated in magnetite, both Ni and V are distributed in magnetite and ilmenite according to a factor close to 4:1. Co shows a little preference for ilmenite, but is not especially enriched in the oxides. The only major deviation is shown by M 1044, the ilmeno-norite dike, in which the distribution factor of V between magnetite and ilmenite is close to 1:1. This is probably explained by the high percentage of Fe^3 in the ilmenite, and it may indicate that V substitutes for Fe^3 rather than for Ti. The ratio Fe^3:V in the ilmenite concentrate shows little variation, 40:1 in M 3331, M 868 and M 1044, and 55–60:1 in M 852 and M 1046, where as the ratio Ti:V in the same concentrates ranges between 240:1 and 45:1.

Cu is not enriched in the oxides, except for the magnetite of SM 1106. Generally it is contained in small and scattered grains of chalcopyrite. Mn is highly concentrated in ilmenite. Its distribution factor varies a great deal, probably due to the formation of secondary garnet, which easily picks up Mn. In SM 1106 olivine is also rich in Mn (MnO = 1.3%).

DISCUSSION

For the discussion of the results of this investigation, the papers by Wager and Mitchell (15), Vincent and Phillips (11), and Buddington, Fahey and Vlisidis (1), have been of great value. Of special interest in this connection is the conclusion reached in Buddington's paper, that the range of TiO_2 in magnetite of gabbroic or ultrabasic rocks of igneous origin is 10–25 percent, of metamorphic rocks only 0–5 percent. Of the many important results of the geochemical investigations of the Skaergaard gabbro, the variation of Vanadium in magnetite during the crystal fractionation, is of special application to the present study.

Of the ore deposits considered in this paper, only the Øvre Røddal occurrence demonstrates mineralogical and geochemical relationships that are not contradictary. The primary texture and minerals are of ordinary, igneous kinds. The geochemical character, high Fe^2, Mn and P, low V, the absence of Cr and Ni, and the presence of Zr, demonstrate that the rock is a late intermediate differentiate of a strongly fractionated gabbroic magma. The mineral chemistry confirms this: olivine is a ferro hortonolite, magnetite is too rich in Ti to be a product of metamorphism but not rich enough to be an early differentiate. All of the other chemical data on magnetite and ilmenite are also in accordance; viz., the low V in magnetite and high Mn, low Mg in ilmenite. In this rock, metamorphism has not been strong enough to make important changes in the chemical composition of the ore minerals. Also the ferromagnesian silicates have largely escaped metamorphism. The formation of almandine in plagioclase, however, shows that Fe ions must have been diffusing. Only plagioclase has been really affected, as it has suffered a strong K-metasomatism, turning it into perthite or antiperthite. This, as well as the garnet formation, are regional metamorphic phenomena.

In the opinion of the author, the rock, also the ore, are of igneous origin, and the intrusion is late orogenic (Caledonian).

Since the other three deposits cannot without objections be explained as magmatic products, the possibility of sedimentary origin, may be considered. When the trace elements of the Sunnmøre series are compared with those given by Krauskopf (9) for different series of sedimentary rocks, it is seen that especially Cr, Ni and V, are much higher. Only black shales and sedimentary iron ores may show figures as high as that. Certainly, the Sunnmøre ores were not originally black shales, and their content of Ti as well as other major elements is rather different from sedimentary iron ore. In general, it may be safely assumed that, if of sedimentary origin, the ores and rocks must have suffered strong metasomatism.

The Øyen occurrence, in the same geographic and geologic environments as Øvre Røddal, has a completely metamorphic character, texturally as well as mineralogically. The high content of Cr, concentrated in the magnetite, indicates an early magmatic origin, but the low Mg in the bulk analysis, and the relatively high Mn in ilmenite, may not support this theory. Of the ore minerals, magnetite especially seems almost entirely recrystallized, and the Ti content, accordingly, is very low. Still the Fe^2 content of ilmenite, now present in exsolved hematite blebs, is rather high. The chemistry of the ore minerals is somewhat like that of the ore minerals in the anorthosite-segregations, and since the surrounding plagioclase rich gneiss may well be an altered anorthosite, it is possible that the ore is related to an original anorthosite. If so, the genetic problem still is not solved, only transferred to the anorthosite problem.

The formation, or the recrystallization of the Øyen ore took place in a (high rank?) amphibolite facies. Later, it was affected by a strong retrograde metamorphism of epidote-amphibolite or greenschist facies. It is possible that the sulfides, which are present in greater abundance than in other ores of this type in the district, are connected to this younger facies, since they appear to be younger than the oxides.

The Verkshaugen deposit is another puzzle. It also shows abundant metamorphic structures, although it is possible that the olivine, enstatite and ore minerals are relics of an original igneous rock. If so, probably the ore-rich bands represent ilmenite-magnetite-olivinite bands within a gabbro or dolerite, in analogy with the Taberg titaniferous iron ore in Sweden (6) The remarkable enstatite-magnetite intergrowth may be of either primary (late magmatic), or secondary origin. The mineralogical relationships indicate that olivine, enstatite and iron oxides have crystallized in the same period, olivine may have been a little ahead of the others. Whether garnet has been formed at this stage, or later, cannot be definitely concluded, since garnet during retrograde metamorphism may have developed a wide reaction zone, which has completely destroyed the original relationship. Garnet most probably belongs to an early period of metamorphism, when the eclogite surrounding the ore bands was formed. Diopside and hornblende may belong to the retrograde metamorphic period, when the omphacite of the eclogite was transformed to a symplectite of plagioclase, diopside and hornblende.

Most of the geochemical data are in conformity with the hypothesis of an

early magmatic formation of the ore-olivinite. The chemical composition is very close to cumberlandite, and magmatic ore-olivinites of other areas. Olivine, enstatite, magnetite and ilmenite are all Mg-rich. In magnetite, Ni also is high. Cr, however, is not especially high, and Ti in magnetite so low that if it is a magmatic mineral, the original Ti content has mostly been expelled.

The greatest obstacle to the magmatic theory in this case, is the bands of garnetfels, which alternate with the ore-olivinite. They must be rather high in Al, and might be interpreted as metamorphic sedimentary layers. But the complete lack of alkalies, (only a little Na is present in the eclogite) is an even greater obstacle to the sediment theory. Generally the rock is not extremely high in Al (cf. the analyses of the eclogite) and since the garnet bands are not thicker than 1 dm, they may be the result of metamorphic differentiation.

In the authors opinion, the eclogites of Sunnmøre are products of regional metamorphism (3). Some of them, possibly the majority, occur in the reaction skarn zones in connection with marbles, and most probably the original rock was some kind of marl. Olivine is not reported from the reaction rocks in the district, but it seems that the metamorphic facies was somewhat higher in the westernmost part, in which Verkshaugen is located. Other eclogites are metamorphosed igneous rocks. The geochemistry of such metamorphic rocks is not well known, and a final decision on the origin of this deposit cannot be reached until more field and laboratory work is done.

The genesis of the titaniferous iron ores of anorthosites is closely connected to the genesis of the anorthosite itself, a matter which is still not definitely settled. It can be studied better in other places than Sunnmøre where the anorthosites, (Fiskå included), have been subjected to a strong metamorphism after the emplacement.

The Fiskå ores are characterized by stronger Ti-enrichment and higher oxidation of the iron than the other deposits included in the present study. The noritic dike ore is most extreme in Ti-enrichment, the segregation ore in oxidation of iron. As seen from the composition of the rhombic pyroxenes and the Cr-values, the dike rock may represent a later differentiate than the segregations, which probably are contemporaneous with the anorthosite. Also the ilmenite of the dike is lower in Mg than that of the segregations. The generally high Cr in both ore types is an interesting feature. It could possibly indicate that the anorthosite is an early differentiate of a basaltic magma (which under orogenic conditions may yield dunites, and anorthosites) (cf. 4, p. 112). The high oxidation state of iron indicates high water vapor pressure existing during crystallization. The remarkable giant crystals of the anorthosites, one of the greatest puzzles of the anorthosite problem, may also be explained similarly.

Ramberg (10) and de Vore (2) have advanced theories of formation for titaniferous iron ores by metasomatism (diffusion). Their ideas are, however, rather controversial, Ramberg thinks that ilmenite is formed by Ti which is liberated from hydrous ferromagnesian silicates, mainly hornblende, during their transformation to pyroxene in granulite facies. Accordingly, the

ore should be formed by *progressive* metamorphism. De Vore, however, suggests that the ore is formed by *retrograde* metamorphism, since the femic minerals (again especially hornblende) in granulite facies is much higher in Ti than those of amphibolite and epidote-amphibolite facies. For the titaniferous iron ores in anorthosite, Ramberg advocates the idea of long range diffusion in the gravitational field, since he does not believe that the Ti-source is to be found within the anorthosite. Ti liberated by mineral transformations elsewhere, will tend to migrate downwards into an anorthosite shell, which he believes to exist at a certain depth. De Vore suggests that the source of Ti is the opaque microlites in the giant feldspar crystals. During granulation and recrystallization, which, according to him, take place in granulite facies, the microlites disappear, and his spectrochemical analyses indicate that the granulated zones contain less Ti than the original crystals. Ti thus liberated diffuses and forms the orebodies in structurally favorable places.

Ramberg no doubt is right that ilmenite may be formed in granulite facies during transformation of certain ferromagnesian silicates, provided quartz is present in sufficient quantities. However, in almost all the gabbroic rocks, within which titaniferous iron ores are formed, there is no such surplus of quartz. On the contrary, some are rather undersaturated. De Vore does not take into consideration that Ti liberated from the feldspar crystals may be taken up in minerals like hornblende, sphene, and biotite, which generally are formed during the recrystallization of anorthosites (which does not necessarily have to take place under granulite facies conditions). Another obstacle noted by de Vore, is that iron is concentrated, not leached, in the granulated zones. Thus, another source of iron must be postulated.

The real problem of the formation of titaniferous iron ores is not the origin of Fe and Ti, (both are abundant metals especially in basic magmas) but the concentration mechanism of the ores. The metasomatic theories of the formation of titaniferous iron ores in anorthosite are at a loss to explain the igneous looking ilmeno-norite dikes so often encountered in ore-bearing anorthosites.

The present author has, in his studies of the Sunnmøre ore deposits, certainly not excluded the possibility of formation by metasomatic processes. In exceptional cases, e.g., in the dike ore at Fiskå, the oxides seem to replace a few primary minerals, especially apatite. This may also be explained as a late magmatic phenomenon, especially since the dike in all other respects seems to confirm a magmatic origin. Generally the oxides fill interstices between the earliest minerals, or exhibit mutual contacts (e.g., with pyroxene). During the regional metamorphism, the ore minerals, also in the dikes, are replaced by hornblende, garnet, and biotite, and to some extent by leucoxene. In a few cases, and to a limited extent hematite replaces magnetite during this metamorphism. *Generally, in Sunnmøre the metamorphism tends to reduce the amount of ore minerals.* The fact that the titaniferous iron ores in Sunnmøre occur in so many different host rocks may be taken as an indication of ore formation related to the regional metamorphism. This, again, raises the question as to why the deposits exhibit such a variation in geochemistry, especially of trace elements. Although trace element distribution during regional metamorphism is not well known, one might expect a more uniform trace ele-

ment distribution in minerals formed under the same PT conditions. As stated elsewhere, there is very little variation of metamorphic facies in Sunnmøre.

In the ores and rocks of the present study, another difficulty in accepting a theory of metasomatic formation, is the lack of relics related to an eventual progressive (or early) metamorphism. In almost every case, when two or more generations of minerals are present, Ti-Fe oxides belong to the oldest generation. This does not exclude the possibility of metasomatic formation, but it makes such a theory rather hypothetical.

CONCLUSIONS

The mineralogical and geochemical study of the four titaniferous iron ore bodies in Sunnmøre has lead to a clear conclusion of the genetic problems for only one of them, the Øvre Røddal ore-rich olivine gabbro, which is a late intermediate differentiate of a strongly differentiated basaltic magma. It was intruded rather late during the orogenesis, whereas the other three were formed at an earlier stage, and therefore are more thoroughly metamorphosed.

The author is inclined to believe that the Fiskå anorthosite and its two types of ilmenite ore are magmatic products. Most of the geochemical data, furthermore, of the Verkshaugen ore-olivinite in eclogite seem to indicate a magmatic origin. Especially the last one has been thoroughly metamorphosed, and few, if any, primary minerals and structures have survived. The Øyen occurrence does not exhibit any igneous structures, and the geochemical data are rather controversial. Thus, it is possible that it is formed by metasomatism. When the general effect of metamorphism upon the ore minerals is considered, formation by metasomatism must be referred to an even earlier metamorphic stage, traces of which are not easy to find.

The other titaniferous iron ores in Sunnmøre are connected with mafic rocks, and at least one (the Solnør-Sjøholt deposit) is a differentiation product of a basaltic magma, which has formed a great number of dolerites (4). Thus magmatic differentiation has played an important role in the formation of such ores in the district. ***In no case, to my knowledge, has the formation of ore been attained by concentration of early magmatic crystals.*** The ore minerals are formed later than olivine and most plagioclase, contemporaneous with pyroxene, and probably earlier than orthoclase (4, p. 86). Many features would be explained best if the ore material was concentrated by liquid immiscibility.

If most of the titaniferous iron ores described above have been formed by magmatic processes, the metamorphism has affected the ore minerals rather differently. With the exception of the Øvre Røddal ore, most of the TiO_2 content, which should be in the range 10–25 percent, has been expelled from the original titaniferous magnetite and transferred to ilmenite or other minerals. The hematite exsolution bodies of ilmenite, however, are in place, and to a large extent ilmenite also seems to have preserved the original Fe-Mg-Mn relationship. In both ore minerals, most trace elements seem to be quite stable during metamorphism.

The question may arise why the district is so rich in deposits of titaniferous iron ore. The tectonic position of the rocks may give the answer. The gabbroic intrusions occurred at a considerable depth during the (Caledonian) orogeny. Thus the cooling of the magmas would be fairly slow, and the conditions favorable for strong differentiation.

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NORGES GEOLOGISKE UNDERSÖKELSE,
OSLO, NORWAY,
Feb. 21, 1957

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OCCURRENCE OF SELENIUM IN SULFIDES FROM SOME SEDIMENTARY ROCKS OF THE WESTERN UNITED STATES[1]

R. G. COLEMAN AND MARYSE DELEVAUX

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ABSTRACT

Investigations of the minor- and trace-element content of sulfides associated with uranium ore deposits from sandstone-type deposits have shown that selenium commonly substitutes for sulfur. The Morrison formation and Entrada sandstone of Jurassic age and the Wind River formation of Eocene age seem to be seleniferous stratigraphic zones; sulfides deposited within these formations generally contain abnormal amounts of selenium. The selenium content of the pyrite, marcasite, and chalcocite is much greater than that reported in previously published data.

Under the prevailing temperatures and pressures of formation of the Colorado Plateau uranium deposits the maximum amount of Se substituting for S in the pyrite structure was found to be 3 percent by weight. Ferroselite, the iron selenide ($FeSe_2$), was found in two deposits on the Colorado Plateau and it was also established that galena (PbS) forms an isomorphous series with clausthalite (PbSe) in nature.

During oxidation of the selenium-bearing sulfides and selenides from the Colorado Plateau and Wyoming, the selenium forms pinkish crusts of either monoclinic or hexagonal native selenium intergrown with soluble sulfates, suggesting that under "normal" oxidizing conditions native selenium is more stable than selenites or selenates.

[1] Publication authorized by the Director, U. S. Geological Survey.

The above-normal selenium content of these sulfides from sedimentary rocks of Mesozoic and Tertiary age is significant. The high selenium in these sulfides is related to periods of volcanic and intrusive activity penecontemporaneous with the formation of the containing sediments.

INTRODUCTION

MINERALOGIC studies of the Colorado Plateau uranium deposits, conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission, reveal a rather persistent association of selenium with these uranium deposits. The unique geochemical character and restricted occurrence of selenium make it an indicator element that can be used as a tool for interpretation of the processes that have given rise to these ore deposits. The first mention of the association of selenium with these ore deposits was given by Beath (2), who has shown that selenium-bearing plants are consistently present where the Morrison formation of Jurassic age crops out. Cannon (8, 9, 10) in more recent studies has used selenium-bearing plants as prospecting guides in the location of uranium deposits on the Colorado Plateau. Shoemaker and others (written communication) in their minor-element study of several hundred mill pulps from producing uranium mines, show that selenium has been concentrated in the ores from sandstone-type uranium deposits.

The purpose of this investigation was to determine the nature and amount of selenium within the ore deposits and to establish its distribution with respect to the ore bodies and their host stratigraphic units. To do this the sulfide minerals were chosen as the best possible means of detecting selenium present in the ores. Goldschmidt and Hefter (19) have shown that sulfur and selenium are very closely related in ionic size and that commonly selenium substitutes for sulfur in sulfide minerals.

Pyrite is almost universally associated with the unoxidized ore bodies from the Colorado Plateau and was chosen as the best mineral to test the distribution of selenium. Where pyrite was not found, galena, chalcocite, and chalcopyrite were tested. The sulfur/selenium ratio of sulfides has been used by several workers to distinguish between ore deposits of sedimentary or hydrothermal origin. Goldschmidt and Strock (20) have shown that pyrite formed during diagenesis of sedimentary rocks has a S/Se ratio of 200,000 or more, and pyrite of hydrothermal origin has a S/Se ratio of 10,000 to 20,000. Carstens (7) found that sedimentary pyrite from Norway contained less than 1 ppm Se as compared to 20 to 30 ppm in pyrite from hydrothermal deposits. A more recent comprehensive study by Edwards and Carlos (15) on the selenium content of Australian sulfides shows a similar genetic relationship. They restrict the use of the S/Se ratio to those provinces that generally have a low selenium background and have picked pyrite or marcasite or both as the most satisfactory index sulfides. Edwards and Carlos assume that when the S/Se ratio is equal to or less than 10,000 the deposit containing pyrite and/or marcasite may be of hydrothermal origin. Applying this concept to certain ore deposits associated with particularly persistent stratigraphic horizons, Edwards and Carlos infer that these deposits are hydrothermal and not

of sedimentary origin on the basis of the S/Se ratio of the sulfides from these deposits.

This interesting relationship may be valid for the Australian deposits if it can be shown that all of the selenium was derived from mineralizing solutions originating at depth, but Edwards and Carlos do not indicate what the S/Se ratio may have been in pre-ore (diagenetic) sulfides from the host stratigraphic units. These inferences regarding origin based on S/Se ratios must be used with great care unless one knows the selenium content of the host rock before mineralization. For instance, the uranium deposits of the Colorado Plateau region of the western United States occur in persistent sandstone units that are known to have an exceptionally high background in selenium as pointed out by Beath (2) and Trelease and Beath (32); therefore, one would expect sulfides forming during diagenesis or later in such a host rock to contain Se indigenous to the rock and here it would be difficult to determine the source of the selenium—that is, sedimentary or hydrothermal.

METHODS OF MINERAL SEPARATION

To insure pure samples for selenium determinations, special precautions were taken using several unusual separatory techniques. The samples containing sulfide were crushed fine enough to release the sulfide from the gangue material and then elutriated to remove the clay-size fraction (little or no sulfide was lost in the elutriate). The sulfide was then separated from the gangue by flotation using a Mayeda cell (22). The advantage of the Mayeda cell is the small quantity of material that can be used. Satisfactory separations were obtained on 10-gram samples containing less than 1 gram of sulfide. The sulfide concentrates obtained from flotation were then centrifuged in bromoform to remove the lighter gangue.

For pyrite and marcasite further purification of the concentrate was effected by treatment with warm concentrated hydrochloric acid to remove oxidation products and carbonates; when silicates remained the concentrate was further treated with warm hydrofluoric acid. Tests have shown that pyrite and marcasite are unharmed by warm hydrochloric and hydrofluoric acid (1, 21); however, the other sulfides analyzed, such as galena, chalcocite, and chalcopyrite were not acid treated. The superpanner was used to effect further purification with these sulfides. Almost all of the samples analyzed were at least 95 percent pure. X-ray and spectrographic determinations on each sample were made to determine what impurities remained, if any. Quartz and barite were the most common impurities, and it was felt that these minerals would not alter the ultimate selenium determinations.

PROCEDURE FOR THE DETERMINATIONS OF SELENIUM IN SULFIDES

The method for the determination of selenium is based on the widely used distillation of selenium tetrabromide, particularly as described by Robinson and others (27). A 1-gram sample of the sulfide is transferred to the distillation flask and is decomposed with nitric acid. The selenium is distilled with a solution of hydrobromic acid and bromine. The distillate is treated

with a slow stream of sulfur dioxide to reduce the free bromine to hydrogen bromide, and hydroxylamine hydrochloride is added to precipitate the selenium in its elemental form. The selenium is then determined colorimetrically or gravimetrically.

For the colorimetric estimation, an aliquot of the distillate containing 3 to 100 micrograms of selenium is used, and estimation is made visually against a series of standards containing 5, 10, 20, 30, 40, 50, 75, and 100 micrograms of selenium. For samples containing more than 0.2 mg of selenium, the precipitated selenium is filtered, dried, and then weighed on a semi-micro balance. The chemical analyses were made by the junior author.

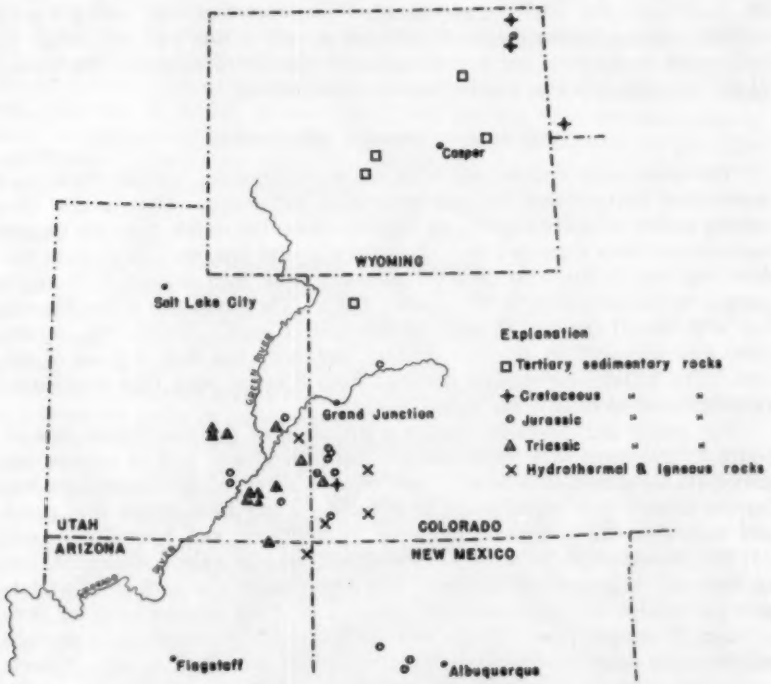


FIG. 1. Locations of samples.

GEOLOGIC AND GEOGRAPHIC DISTRIBUTION OF THE ANALYZED SULFIDES

Most of the sulfide samples studied were taken from uranium and uranium-vanadium ore deposits in sedimentary rocks. The Colorado Plateau region was sampled extensively and here most of the uranium deposits are within several persistent stratigraphic units; the Morrison formation of Jurassic age, Entrada sandstone of Jurassic age, Todilto limestone of Jurassic age, and

Chinle formation of Triassic age. Outside the Colorado Plateau, samples were tested from uranium ore deposits and associated sediments within the Tertiary sedimentary rocks of Wyoming, particularly the Wasatch and Wind River formations of Eocene age. In the Black Hills area of South Dakota and Wyoming, sulfides were analyzed from the Fall River sandstone, Fuson shale, Minnewaste limestone, and Lakota sandstone, all of Cretaceous age. Other samples from nonuranium-bearing sediments and igneous rocks from the western United States were also tested to establish the general selenium background. The location of these samples is shown in Figure 1.

FORM AND OCCURRENCE OF THE SULFIDES

Pyrite and marcasite are the most abundant sulfides associated with the uranium deposits and commonly form fine disseminations or nodular concretions. In most of the deposits pyrite was found to be more abundant than

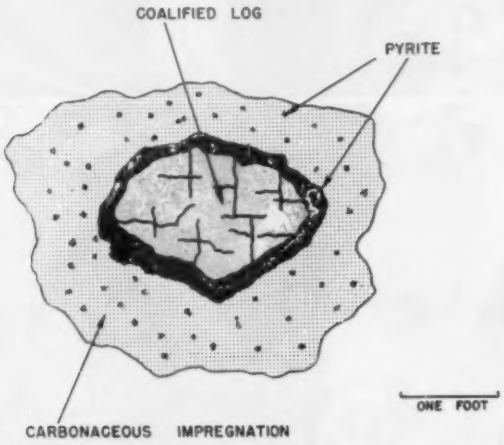


FIG. 2. Coalified log showing typical sulfide concentration.

marcasite. Where sulfides have been precipitated within carbonaceous material, they assume the structure of the woody material which they replace (Fig. 2).

The sulfides have been divided into two types according to their position with respect to the unoxidized uranium-vanadium ore deposits. The relatively abundant sulfides taken from within the ore or following the outline of the ore bodies are considered as ore sulfides (rock containing > 0.01 percent U_3O_8). There is no evidence to suggest that the uranium deposits in sandstone-type deposits are accompanied by a surrounding zone of sulfides away from the ore, as is commonly found in hydrothermal vein-type deposits. The ubiquitous and scattered sulfides in the unmineralized rock show no relationship with the ore bodies and are considered barren sulfides. It is assumed that

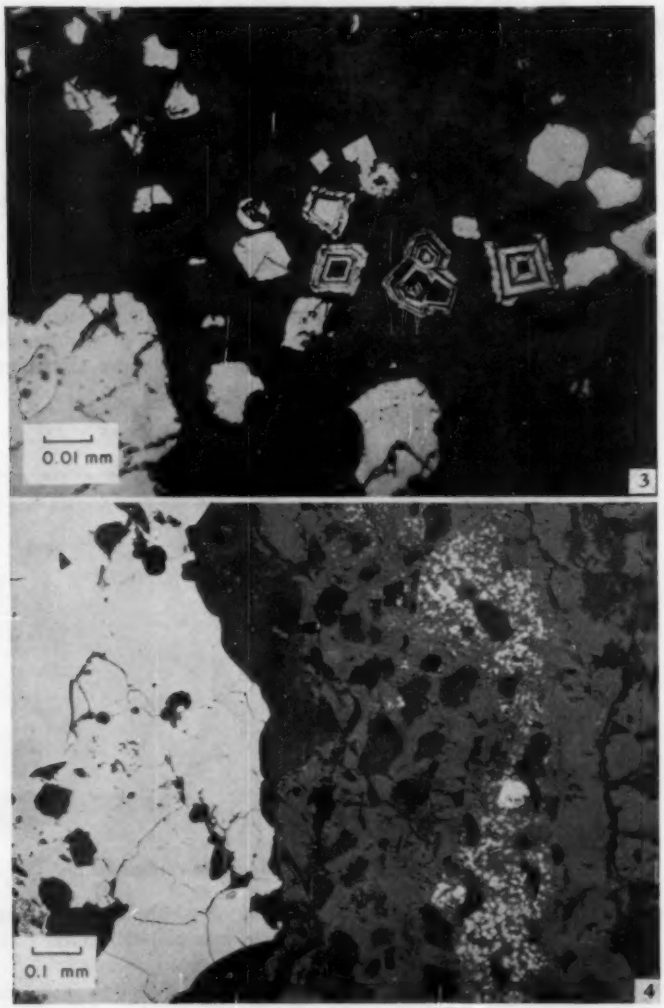
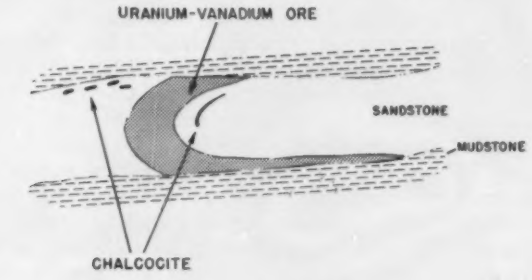


FIG. 3. Pyrite associated with uraninite and coffinite. The mottled dark-gray groundmass is an intimate mixture of uraninite and coffinite. Zoned crystals of pyrite show selective replacement by galena, uraninite, and coffinite. The light irregular patches are also pyrite and they show strong corrosion by the uranium minerals. Mi Vida mine, Monticello district, San Juan County, Utah. Polished section, plain light.

FIG. 4. Pyrite associated with uraninite. Massive pyrite on the left is replaced by calcite. Light-colored zoned crystals in the uraninite (medium gray) are second-generation cobalt-rich pyrite. A band of sphalerite is along the right-hand border of the picture. Hidden Splendor mine, San Rafael district, Utah. Polished section, plain light.

most of the sulfides in the barren rock formed independent of and prior to the deposition of the uranium-vanadium ores either during diagenesis or later from nonuraniferous circulating intrastratal solutions. The sulfides within the ore are considered to have formed from the fluids transporting the metals for the uranium deposits or by reconstitution of the pre-ore sulfides by these fluids or



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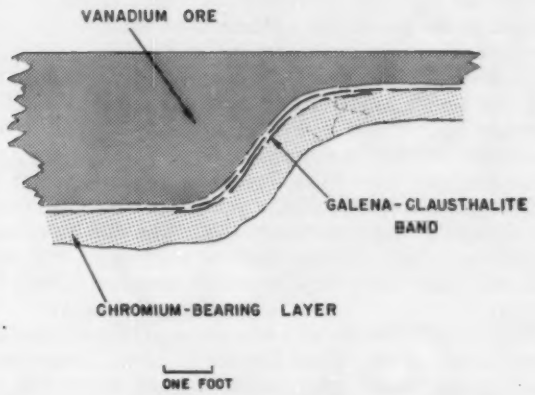

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FIG. 5. Roll ore body and associated sulfides, Morrison formation.
FIG. 6. Galena-clausthalite band and its relationship to vanadium deposit in Entrada sandstone.

by both (Figs. 3 and 4). This division is arbitrary as there is difficulty in establishing criteria to distinguish early sulfides from those sulfides produced by the later ore-bearing fluids.

The presence of iron sulfides has been recorded in many drill cores of unoxidized barren rocks from the Morrison and Chinle formations on the Colorado Plateau and from the Wind River formation in Wyoming. Shawe (29) has

shown that two types of diagenetic changes have taken place in the sedimentary rocks of the Colorado Plateau prior to uranium mineralization: 1. oxidation, producing hematite and the characteristic red coloration, 2. reduction, producing iron sulfides and the characteristic green coloration. Thus it seems likely that iron sulfides must have formed in these sediments where reducing conditions existed before ore deposition. Another line of evidence suggesting two distinct periods of iron sulfide deposition has been found in the Ni: Co ratio of these sulfides. Hegemann (21) and Talluri (30) have shown that pyrites formed by sedimentary processes generally have Ni > Co and those pyrites formed by hydrothermal processes generally have Co > Ni. Exceptions to this general rule are common, but the senior author has found that the barren iron sulfides used in this study usually show Ni > Co and those from the ore have Ni < Co. This illustrates that the division of the sulfides into barren and ore groups reflects a change in composition of the sulfides which probably results from different environments of deposition. Undoubtedly some of the sulfides are placed in the wrong group because the collection of these samples was based primarily on their position as related to the ore bodies described above; however, this classification is convenient to illustrate the partition of the selenium in sulfides with respect to the uranium deposits.

The chalcopyrite, chalcocite, and galena deposited in the uranium ores are probably formed by the ore fluids, as there is no geologic evidence to prove that they are pre-ore. Pyrite and marcasite seem to be the only early sulfides.

The most unusual characteristic of the sulfide deposition with respect to the ore is the thin sulfide bands that follow the outline of the roll ore bodies. These roll ore bodies, described by Fischer (16), are layered deposits that cut across the sandstone bedding in sharply curving forms (Figs. 5 and 6). The sulfides within the band have been deposited interstitial to the sand grains (Fig. 7) and the band is usually characterized by a monomineralic sulfide—either pyrite, chalcocite, or galena-clausthalite. The sulfides within the bands usually have extremely high selenium contents, as much as 18 percent. Shawe (28) believes that these sharp depositional features were formed at a static interface between fluids of different composition and density.

The coalified wood within the deposits seems to have controlled to a large extent the precipitation of the ore and also the sulfides. Larger coalified wood fragments and logs contain abundant sulfide that may completely replace parts of the wood preserving the cell structure (Figs. 8 and 9). The pyrite also commonly forms an aureole around the log as fine disseminations in the containing sandstone (Fig. 2). The more prevalent tabular ore bodies contain sulfides disseminated throughout with marked concentrations at the boundaries of the bodies, and within the bodies small carbonaceous fragments show strong localization of sulfide.

Selenides are common in the ores from the Morrison formation and Entrada sandstone and extremely rare in the ores from uranium deposits in rocks of Triassic age. Clausthalite (PbSe) is the typical selenide found, and in the vanadium deposits from the Rifle and Garfield mine, Garfield County, Colo., a persistent sulfide band contains clausthalite-galena in variable amounts; the band can be traced for several thousand feet along the strike of the deposit.

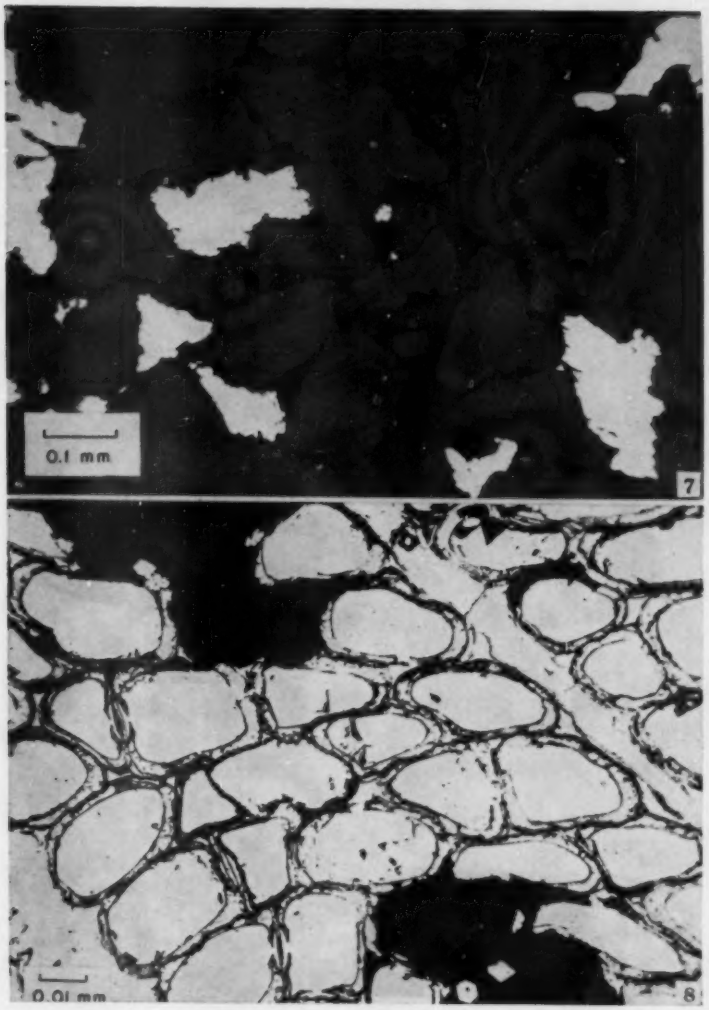


FIG. 7. Galena-clausthalite band. Galena-clausthalite (white) interstitial to detrital quartz grains; other intergranular areas between the quartz are filled with clay minerals. Rifle mine, Rifle district, Garfield County, Colo. Polished section, plain light.

FIG. 8. Pyrite (white) impregnating and replacing wood structure. Black interstitial areas consist of quartz and relict carbonaceous material. Marshbank Canyon claim, San Rafael district, Emery County, Utah. Longitudinal polished section, plain light.

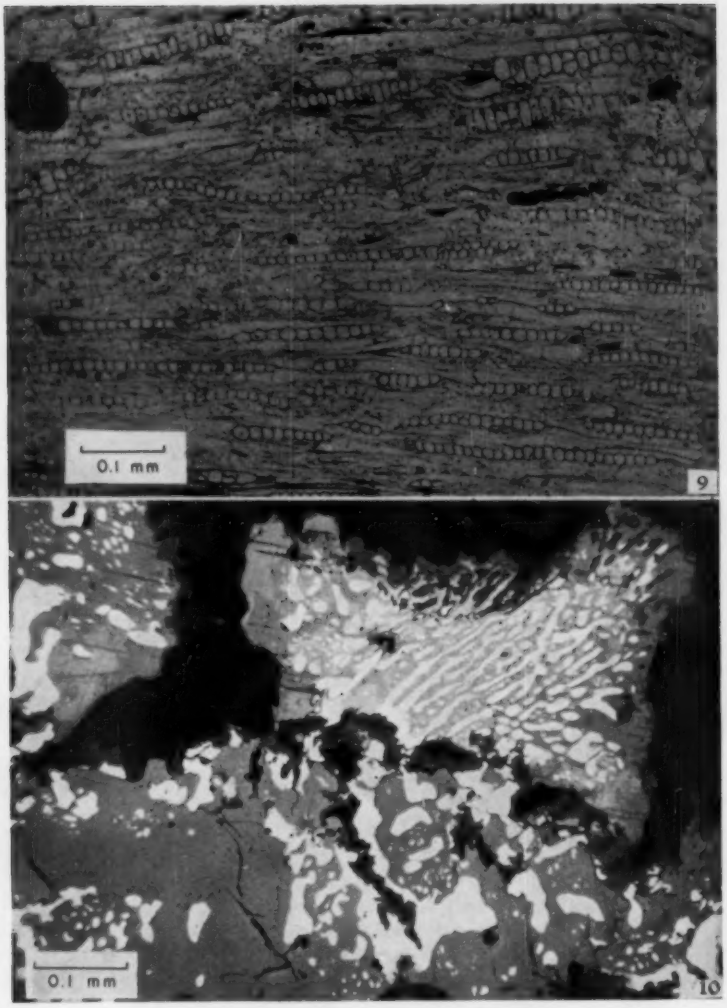


FIG. 9. Pyrite (gray) impregnating and replacing wood structure. Black areas are carbonaceous material. Hideout mine, White Canyon, San Juan County, Utah. Transverse polished section, plain light.

FIG. 10. Chalcocite nodule containing intergrowths of clausthalite (white) and chalcocite (medium gray) surrounded by embayed quartz (dark gray). Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

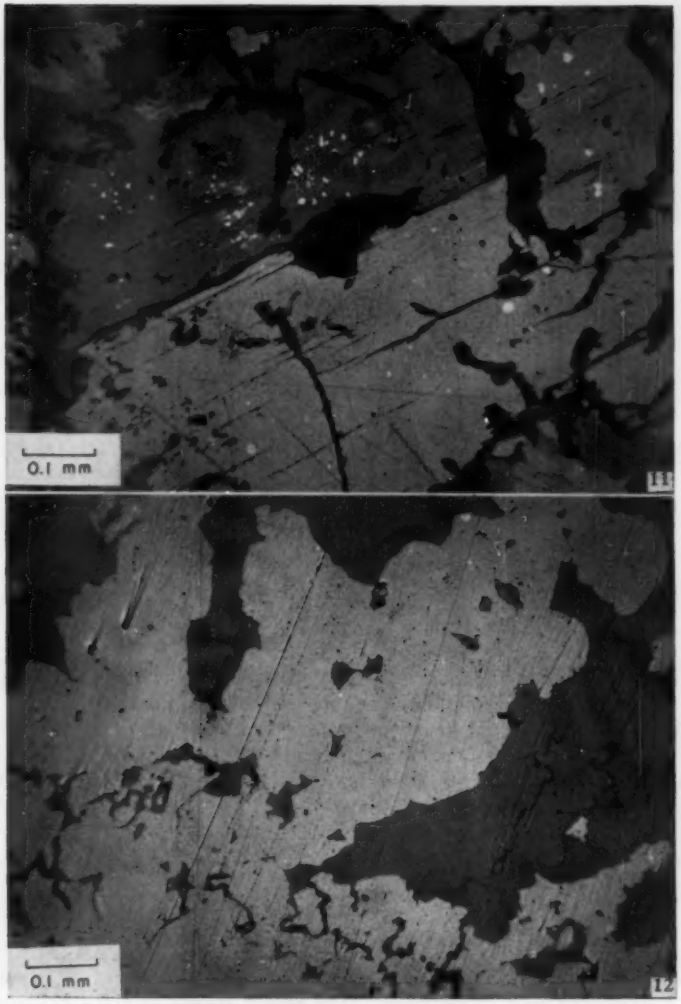


FIG. 11. Chalcocite (light gray) and digenite (medium gray) containing small inclusions of clausthalite (white). Alteration (oxidation) along irregular veins (black to dark gray) produces secondary copper vanadates and carbonates. Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

FIG. 12. Clausthalite (light gray) and eucairite (dark gray) in central part of chalcocite nodule. Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

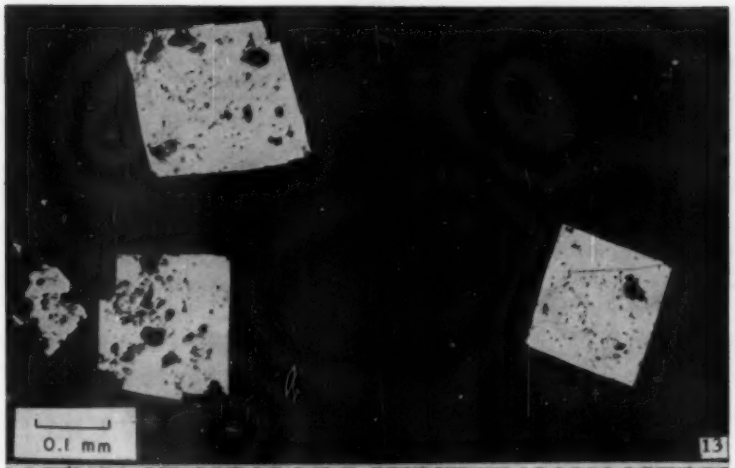
An exceptional concentration of clausthalite was found (Lee Eicher, U. S. Geological Survey, personal communication) in the Corvusite mine, Montrose County, Colo. Here a wide band of clausthalite formed a semicircular band around a large log (18 in. in diameter and about 10 ft. long) representing the largest concentration of selenide yet found on the Colorado Plateau. An unusual occurrence of clausthalite is found in chalcocite nodules from the Cougar mine, San Miguel County, Colo. Clausthalite is intergrown with chalcocite (Cu_2S) and digenite ($Cu_{2-x}S$) (Figs. 10, 11), and in some nodules the rare selenide, eucairite (CuAgSe) (Fig. 12) is associated with the chalcocite and clausthalite. Ferroselite (5), the iron selenide $FeSe_2$, is the only selenide so far identified in Triassic deposits. In the Triassic it has been found only in the Chinle formation in the Temple Mountain area, where it occurs in the AEC No. 8 mine, Emery County, Utah, associated with pyrite and coalified wood. In the Morrison formation of Jurassic age ferroselite has been found at the Virgin No. 3 mine, Montrose County, Colo., by D. R. Shawe of the U. S. Geological Survey.

The sulfides in barren rock from the Colorado Plateau are present within mudstones and standstones, usually as nodular masses, small euhedral crystals (Fig. 13), or as concretions. In mudstones the pyrite and marcasite usually form larger crystals and tend to be more euhedral, whereas in sandstone these sulfides are anhedral to subhedral filling the interstitial areas. Marcasite and pyrite seem to be of equal abundance in these rocks. Barren coalified wood contains abundant sulfide and some of the sulfide in mineralized coalified wood fragments within the ore has formed before the deposition of the uranium ore; some of it may have been reconstituted by the ore fluids or may have been unchanged by these processes of ore deposition (Fig. 14).

Sulfides from the Tertiary uranium deposits in Wyoming do not exhibit the unusual distribution found in the sulfides from the Colorado Plateau. The sulfides from these Tertiary deposits are present as extremely fine disseminations in sandstone and in some areas are concentrated along bands formed by secondary enrichment. The sulfides in barren rock form small concretions within mudstones and irregular nodular masses in the sandstone. Marcasite and pyrite are the only sulfides yet found associated with these Tertiary deposits; selenides have not been reported.

DISTRIBUTION OF SELENIUM IN THE SULFIDES

In the early stages of this investigation it became apparent that the sulfides deposited in the sedimentary rocks of the Colorado Plateau and Wyoming were exceedingly high in selenium. The recent survey of trace elements in sulfides by Fleischer (17) shows that the highest selenium recorded in 124 pyrites and/or marcasites from all types of deposits was 300 ppm. Bergenfelt (4) provides an example of a selenium-rich province in the Skellefte district, Sweden; however, even the maximum contents he records for the sulfides from this district are not comparable to those determined in the present investigation. Sulfides from the Boliden mine, Skellefte district, show the following maximum selenium contents: lead-bismuth-antimony sulfides, 6.4 percent Se;



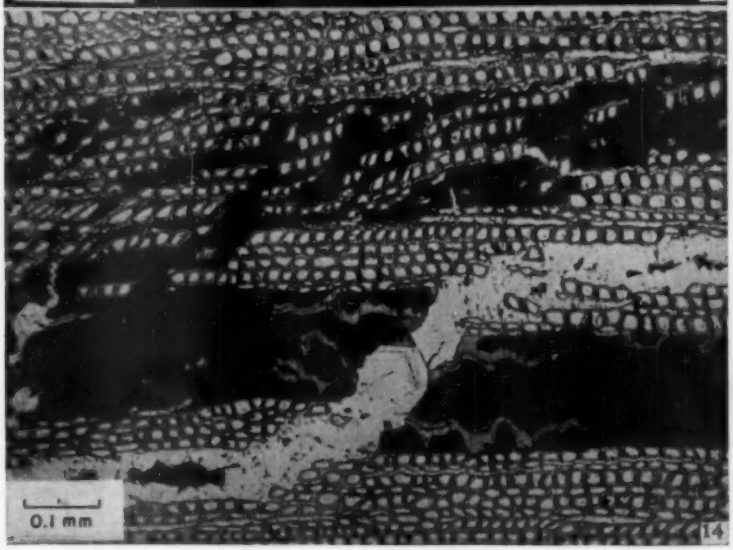


FIG. 13. Euhedral pyrite cubes in barren siltstone underlying mineralized sandstone. Rifle mine, Garfield County, Colo. Polished section, plain light.

FIG. 14. Mineralized log showing wood structure with the cell walls replaced by marcasite and the lumens (cell cavities) impregnated by pyrite-marcasite. Second generation of pyrite (white vein), calcite (black), and galena (medium gray) cutting and displacing the woody structure. Adams Uranium Co. mine, San Rafael district, Emery County, Utah. Polished section, plain light.

TABLE 1

SELENIUM CONTENT OF SULFIDES FROM SEDIMENTARY ROCKS OF JURASSIC AGE

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
Morrison Formation			
Uravan dist., Montrose Co., Colo.			
1. North Star mine	pyrite	O	0.014
2. Virgin No. 3 mine	pyrite	O	0.009
3. Long Park No. 1 mine	pyrite	B	0.039
4. Long Park No. 1 mine	pyrite	B	0.001
Gypsum Valley dist., San Miguel Co., Colo.			
5. Pitchfork mine	pyrite	B	0.019
Monticello dist., San Juan Co., Utah			
6. Basin No. 1 mine	pyrite	O	0.19
7. Cottonwood No. 3 mine	pyrite	O	0.065
8. Found claim	pyrite	B	0.025
Thompsons dist., Grand Co., Utah			
9. Little Eva mine	pyrite-marcasite	O	0.003
10. Blackstone No. 6 mine	pyrite	O	0.081
Bull Canyon dist., Montrose Co., Colo.			
11. Mineral Joe mine	pyrite-marcasite	B	0.074
12. Mineral Joe mine	pyrite-marcasite	B	0.39
13. Mineral Joe mine	pyrite-marcasite	O	0.10
14. Mineral Joe No. 2 mine	pyrite	B	0.004
15. J. J. mine	marcasite pyrite	O	0.58
16. J. J. mine	pyrite-marcasite	B	0.20
17. J. J. mine	pyrite-marcasite	O	0.55
18. J. J. mine	marcasite-pyrite	B	0.51
19. J. J. mine	marcasite	O	0.65
20. J. J. mine	marcasite-pyrite	B	0.39
21. J. J. mine	marcasite-pyrite	O	0.13
22. J. J. mine	marcasite (pyrite)	O	0.087
23. J. J. mine	marcasite-pyrite	B	0.21
24. J. J. mine	marcasite (pyrite)	B	0.003
25. J. J. mine	marcasite (pyrite)	B	0.58
Slick Rock dist., San Miguel Co., Colo.			
26. Grant claim	pyrite	O	0.66
27. King No. 4 mine	pyrite	O	0.25
28. Tailholt mine	pyrite (marcasite)	O	0.015
29. Tailholt mine	"chalcocite"	O	0.066
30. Tailholt mine	pyrite	B	0.018
31. Drill core 700 ft depth, U.S.V., Burro Canyon	"pyrite-marcasite"	O	5.00
32. Mucho Grande mine	"chalcocite"	O	1.2
33. Cougar mine	chalcocite	O	1.9
34. Cougar mine	"chalcocite-digenite"	O	1.7
35. Cougar mine	"chalcocite"	O	0.2
36. Cougar mine	"chalcocite"	O	0.13
37. Cougar mine	"chalcocite"	O	4.1
38. Cougar mine	chalcocite	O	4.93
39. Cougar mine	"chalcocite"	O	0.42
40. Cougar mine	"chalcocite"	O	0.18
41. Cougar mine	chalcocite	O	0.45
Grants dist., Valencia Co., New Mexico			
42. Woodrow Pipe mine	pyrite	O	0.001
43. Woodrow Pipe mine	marcasite-pyrite	O	<0.0003

TABLE 1—*Continued*

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
Morrison Formation (continued)			
44. Woodrow Pipe mine	pyrite	B	<0.0003
45. Poison Canyon mine	"pyrite"	O	1.00
Henry Mountains dist., Garfield Co., Utah			
46. Walter's claim	pyrite	B	<0.0003
47. Ellen No. 2 mine, North Wash	pyrite(marcasite)	O	0.10
48. Ellen No. 2 mine, North Wash	pyrite-marcasite	O	0.35
Cortez dist., Montezuma Co., Colo.			
49. Drill core, McElmo Creek	pyrite-marcasite	O	<0.0008
Crook County area, Wyoming			
50. Shannon Oil Company claims	pyrite	B	<0.0003
Entrada Sandstone			
Rifle dist., Garfield Co., Colo.			
51. Garfield mine	marcasite	O	0.021
52. Garfield mine	galena-clausthalite	O	8.66
53. Garfield mine	galena-clausthalite	O	8.1
54. Garfield mine	galena-clausthalite	O	7.09
55. Rifle mine	clausthalite-galena	O	14.2
56. Rifle mine	pyrite	O	0.14
57. Rifle mine	galena-clausthalite	O	11.8
58. Rifle mine	clausthalite-galena	O	18.0
59. Rifle mine	marcasite	O	0.014
60. Rifle mine	clausthalite-galena	O	17.0
61. Rifle mine	clausthalite-galena	O	15.1
Placerville dist., Montrose Co., Colo.			
62. Bear Creek mine	galena-clausthalite	O	10.0
63. Fall Creek mine	pyrite	O	0.41
Todilto Limestone			
Grants dist., Valencia Co., New Mexico			
64. F. O. Manol mine	pyrite	B	0.014
65. Crackpot mine	pyrite	B	0.026

[1] General geographic location of samples shown in Figure 1.

[2] X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

[3] Sulfides divided into two types: O = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

[4] Lower limit of detection is 0.0003 percent Se for a 1-gram sample, when less sample was available the lower limit of detection is correspondingly higher.

galena, 1.4 percent; chalcopyrite, 0.14 percent; arsenopyrite, 0.16 percent; and pyrite 0.03 percent. Derriks and Vaes (13) have found 19 percent Se in vaesite (NiS_2) and 11 percent Se in siegenite from unoxidized uranium ores at Shinkolobwe, but they have not analyzed the associated pyrite for selenium.

In contrast to these published data, the sulfides analyzed for this investigation from the sedimentary rocks of the western United States show the following maximum selenium values: "pyrite," 5 percent; marcasite, 0.65 percent; galena-clausthalite, 18 percent; and chalcocite, 5 percent.

The control on the selenium content of the sulfides from this province seems to be stratigraphic rather than a function of the type of ore deposit—that is, hydrothermal versus sedimentary origin, as suggested by Edwards and Carlos (15) for the Australian deposits. The sulfides from the Morrison formation consistently contain more selenium than those from the Chinle formation, with the exception of the Temple Mountain deposits, Emery County, Utah. The pyrite and marcasite from both the barren and mineralized rock from the Morrison contain much more selenium than the average shown by Fleischer (19), whereas these two types of sulfides from the Chinle deposits have much less selenium.

Sulfides from the Morrison Formation, Entrada Sandstone, and Catskill Formation.—Thirty-nine samples of marcasite or pyrite or both were analyzed from the Morrison formation (Table 1). The average selenium content of the iron sulfides both from barren and mineralized rock is 0.17 percent. The averages discussed are arithmetical and those samples containing Se below the sensitivity of the chemical method (3 ppm for a 1-gram sample) are averaged in as zero. The average selenium content of 20 iron sulfides from mineralized rocks is 0.20 percent and for 18 sulfides from barren rock the average selenium content is 0.14 percent. One pyrite-marcasite sample contained 5 percent Se, but this sample was found to contain clausthalite (PbSe) as an impurity. The selenium content of sulfides from mineralized rock is not significantly higher than that of sulfides from barren rock. It would seem that if most of the barren pyrite is pre-ore, selenium was apparently available in the same relative amounts in sediments of the Morrison formation during pre-ore sulfide formation as during the period of uranium mineralization. Therefore, where reducing conditions existed and iron sulfides have been formed in the Morrison formation, either before ore deposition or in the period of uranium ore deposition, selenium has been concentrated in these sulfides, although the ore fluids may have been enriched in selenium as they apparently have traveled laterally through the Morrison for great distances.

The chalcocite bands and nodules characteristic of the Slick Rock district, San Miguel County, Colo., are restricted to the ore bodies and seem to have formed during the uranium mineralization. Some of these sulfide concentrations have extremely high selenium content for copper sulfides, averaging 1.22 percent Se for 11 samples, with a high of 4.93 percent Se. Study of polished sections of these copper sulfides reveals small inclusions of clausthalite and intergrowths of clausthalite and chalcocite-digenite (Figs. 10, 11). Rarely small concentrations of eucairite (Fig. 12) are present in these copper sulfides. These inclusions of selenides account, in part, for the exceptionally high selenium content of the chalcocite, but much of the selenium is probably substituting for sulfur in the chalcocite structure.

The persistent "galena" band developed in the vanadium deposits within the Entrada sandstone is composed of galena-clausthalite in solid solution (Fig. 6). This band is fairly uniform in composition but progressive variations in selenium along the strike of the band were found. The average selenium content of nine samples of galena-clausthalite from these bands is 12.2 percent with a high of 18 percent (Table 1). In contrast, pyrite and

TABLE 2

SELENIUM CONTENT OF SULFIDES FROM THE CHINLE FORMATION OF TRIASSIC AGE

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
San Rafael dist., Emery Co., Utah			
66. Lucky Strike mine	marcasite	O	0.001
67. Lucky Strike mine	marcasite-pyrite	O	0.03
68. Lucky Strike mine	pyrite (marcasite)	O	0.002
69. Lucky Strike mine	pyrite	B	0.013
70. Adams Uranium Company mine	pyrite	B	0.0006
71. Adams Uranium Company mine	galena	O	<0.0007
72. Adams Uranium Company mine	pyrite (marcasite)	B	<0.0003
73. Adams Uranium Company mine	pyrite	B	<0.0003
74. Hidden Splendor mine	pyrite	B	0.0003
75. Hidden Splendor mine	pyrite	B	0.0005
76. Hidden Splendor mine	pyrite	O	0.003
77. Hidden Splendor mine	marcasite (pyrite)	B	0.003
78. Hidden Splendor mine	pyrite	B	<0.001
79. Hidden Splendor mine	digenite	O	0.0004
80. Hidden Splendor mine	pyrite	O	0.006
81. Hidden Splendor mine	pyrite	O	<0.0003
82. Hidden Splendor mine	pyrite	O	<0.0003
83. Hidden Splendor mine	pyrite	O	0.003
84. Donna B. claims	pyrite	O	0.0003
85. Flop Over mine, Temple Mountain	pyrite	B	0.0005
86. AEC No. 8 mine, Temple Mountain	pyrite	O	0.003
87. AEC No. 8 mine, Temple Mountain	pyrite (marcasite)	B	0.006
88. AEC No. 8 mine, Temple Mountain	pyrite	B	0.006
89. AEC No. 8 mine, Temple Mountain	pyrite-ferroselite	O	23.9
90. AEC No. 8 mine, Temple Mountain	pyrite	O	0.50
100. AEC No. 8 mine, Temple Mountain	pyrite-ferroselite	O	13.6
101. AEC No. 8 mine, Temple Mountain	pyrite-ferroselite	O	40.2
102. AEC No. 8 mine, Temple Mountain	pyrite-ferroselite	O	18.0
103. AEC No. 8 mine, Temple Mountain	pyrite	B	0.002
104. North Mesa No. 9 mine, Temple Mountain	pyrite	O	0.030
104. North Mesa No. 9 mine, Temple Mountain	pyrite (marcasite)	O	0.012
White Canyon dist., San Juan Co., Utah			
106. Happy Jack mine	pyrite	O	<0.0003
107. Happy Jack mine	pyrite-marcasite	B	0.0006
108. Happy Jack mine	pyrite	O	<0.0003
109. Happy Jack mine	"chalcopyrite"	O	<0.0003
110. Happy Jack mine	chalcopyrite	O	<0.0003
111. Happy Jack mine	chalcopyrite	O	<0.0003
112. Happy Jack mine	covellite-bornite	O	<0.0004
113. Blue Lizard mine	pyrite	B	<0.0005
114. Blue Lizard mine	pyrite	O	<0.0003
115. Blue Lizard mine	bornite (chalcopyrite)	O	<0.0004
116. Blue Lizard mine	chalcopyrite	O	<0.0003
117. Blue Lizard mine	chalcopyrite	O	<0.0004
118. McCarthy-Coleman claim	pyrite	B	<0.0003
119. Foley Uranium Company mine	pyrite	B	<0.0004
120. Maybe mine	pyrite-marcasite	O	<0.0003
121. Maybe mine	pyrite	B	<0.0003
122. Maybe mine	pyrite (marcasite)	B	0.0006
123. Gismo mine	bornite (chalcopyrite)	O	0.001
124. Gismo mine	pyrite	O	<0.0005
125. Gismo mine	pyrite	B	0.0003
126. Gismo mine	pyrite	O	<0.0004

TABLE 2—*Continued*

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
127. Okie mine	pyrite	O	0.003
128. Okie mine	pyrite	O	0.002
129. Hideout mine	pyrite	B	0.0015
130. Sandy claim	pyrite	B	<0.0003
131. Notch No. 1 mine	pyrite	B	0.0003
132. Happy Surprise claim	pyrite-marcasite	B	0.0003
Monticello dist., San Juan Co., Utah			
133. Mi Vida mine	pyrite	B	0.0003
134. Mi Vida mine	pyrite	O	<0.0003
135. Mi Vida mine	pyrite	O	<0.0008
136. Mi Vida mine	pyrite	B	<0.0003
137. Mi Vida mine	pyrite	O	<0.0003
138. Mi Vida mine	pyrite	B	<0.001
139. Mi Vida mine	pyrite	O	<0.001
140. Mi Vida mine	pyrite	O	<0.0005
141. Mi Vida mine	pyrite	B	0.0008
142. Mi Vida mine	greenockite	O	0.002
143. La Sal No. 2 mine	pyrite	O	0.0004
Monument Valley dist., Apache Co., Arizona			
144. Monument No. 2 mine	pyrite	B	0.0005
145. Monument No. 2 mine	pyrite	O	<0.0003
146. Monument No. 2 mine	pyrite	B	0.0005
Green River dist., Grand Co., Utah			
147. Shinarump No. 3 mine	pyrite	O	<0.0003
Slick Rock dist., San Miguel Co., Colorado			
148. Unknown mine, Dolores Canyon	pyrite	O	0.0009
149. Unknown mine, Dolores Canyon	pyrite	B	0.0007
150. Hunt No. 2 claim	pyrite	B	0.009

[1] General geographic location of samples shown in Figure 1.

[2] X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

[3] Sulfides divided into two types: O = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

[4] Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample was available the lower limit of detection is correspondingly higher.

marcasite deposited in late fractures spatially associated with these vanadium deposits contain only 0.02 percent Se.

Sandstone collected by H. Klemic, U. S. Geological Survey, from the upper part of the Catskill formation, of Devonian age, Carbon County, Pennsylvania, also contains a thin clausthalite band (about a quarter of an inch thick) in juxtaposition with uranium minerals. Further work is needed to determine the relationship of these unique bands to the uranium.

Sulfides from the Chinle Formation.—The distribution of selenium in sulfides from sedimentary rocks of Jurassic age is not reflected by the sulfides from sedimentary rocks of Triassic age. These sulfides, exclusive of the Temple Mountain uranium deposits, show a much lower selenium content than those from the Jurassic (Table 2). Fifty-five samples of pyrite or marcasite or both from sediments of the Chinle formation of Triassic age have an

average selenium content of 0.0015 percent. The average selenium content of 27 iron sulfides from mineralized rocks is 0.0019 percent and of 28 iron sulfides from barren rock 0.0012 percent. These averages do not include samples from the Temple Mountain deposits. Again, as with the sulfides from rocks of Jurassic age, there is no apparent difference in the selenium content of the barren sulfides as compared to the ore sulfides. This supports the premise that the same relative amount of selenium was available for pre-ore and ore periods of sulfide deposition. The uranium ore deposits in rocks of Triassic age generally contain more sulfide than do the deposits in rocks of Jurassic age, but the former sulfides have not mobilized to form continuous bands but have been more thoroughly disseminated throughout the deposits. The associated copper sulfides (bornite, chalcopyrite, and chalcocite) analyzed for selenium show the same relative amounts of selenium as the iron sulfides (Table 2).

In contrast to the other deposits in rocks of Triassic age, the Temple Mountain deposits have an unusual partition of selenium. The sulfide concentrates from ore in this area contain the highest concentration of selenium yet found in the Colorado Plateau, although the sulfides from barren rock contain the same relative amounts of selenium as the average found in other sulfides from rocks of Triassic age. Eight sulfide concentrates from ore containing ferroselite ($FeSe_2$) from the Temple Mountain deposits average 12 percent Se, whereas four sulfide concentrates from barren rock average only 0.004 percent selenium. Thus at Temple Mountain the sulfide minerals in uranium ore are strongly enriched in selenium when compared to the pre-ore sulfides, suggesting that the ore-forming fluids contained abundant selenium.

Sulfides from Sedimentary Rocks of Tertiary Age.—Sulfides associated with the uranium deposits in Wyoming sedimentary rocks of Tertiary age have also been tested for comparison with the Colorado Plateau uranium deposits. The Wind River and Wasatch formations of Eocene age contain the important uranium deposits of this region. The Gas Hills area in the Wind River Basin, the Pumpkin Buttes area, and Crooks Gap area, all in Wyoming, are the three districts sampled. Fifty samples of pyrite or marcasite or both from these three areas have an average selenium content of 0.04 percent (Table 3).

The iron sulfides from mineralized rock have an average selenium content of 0.087 percent, a marked enrichment over the iron sulfides from barren rock which average 0.0015 percent selenium. Secondary enrichment of uranium has occurred near the ground-water table in the Gas Hills area, and the pyrite from this zone contains as much as 1.5 percent Se. The solutions forming the uranium ore deposits in these sediments were considerably enriched in selenium as compared to the solutions responsible for the formation of sulfides before ore deposition. Marcasite and pyrite are the only sulfides observed in the samples collected from the sedimentary rocks of Tertiary age from Wyoming.

One sample from the Maybell district, Colo. (Table 3, no. 203) also contains significant Se as does a sample from Karnes County, Tex. (Table 3, no. 202).

Sulfides from Rocks of Cretaceous Age.—Sulfides from various sedimentary rocks of Cretaceous age in the western United States have been tested for

TABLE 3

SELENIUM CONTENT OF SULFIDES FROM SEDIMENTARY ROCKS OF TERTIARY AGE

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
Wind River Formation (Eocene)			
Gas Hills dist., Fremont Co., Wyoming			
151. Vitro mine	pyrite	B	0.0008
152. Vitro mine	pyrite (marcasite)	O	0.018
153. Vitro mine	marcasite	B	0.0005
155. Vitro mine	marcasite (pyrite)	B	<0.0003
156. Vitro mine	pyrite (marcasite)	O	0.006
157. Vitro mine	pyrite (marcasite)	B	<0.0003
158. Vitro mine	marcasite-pyrite	B	<0.0003
159. Vitro mine	pyrite (marcasite)	O	0.0009
160. Vitro mine	pyrite	B	0.003
161. Vitro mine	pyrite	O	0.013
162. Vitro mine	pyrite	B	<0.0003
163. Vitro mine	pyrite (marcasite)	O	0.051
164. Vitro mine	pyrite (marcasite)	O	0.0009
165. Vitro mine	pyrite	B	<0.0003
166. Vitro mine	pyrite	B	<0.0003
167. Vitro mine	pyrite	B	<0.0003
168. Vitro mine	pyrite (marcasite)	B	0.0003
169. Vitro mine	pyrite (marcasite)	O	0.005
170. Vitro mine	pyrite	B	<0.0003
171. Vitro mine	marcasite-pyrite	B	<0.0003
172. Vitro mine	pyrite (marcasite)	B	<0.0003
173. Vitro mine	marcasite-pyrite	B	<0.002
174. Vitro mine	pyrite (marcasite)	B	<0.0003
175. Vitro mine	pyrite-marcasite	B	0.0005
176. Vitro mine	pyrite (marcasite)	O	1.5
177. Vitro mine	pyrite	O	0.67
178. Lucky Mc mine	pyrite	O	0.003
179. Lucky Mc mine	pyrite-marcasite	B	0.002
180. Lucky Mc mine	pyrite-marcasite	B	0.004
181. Lucky Mc mine	pyrite	O	0.12
182. Lucky Mc mine	marcasite (pyrite)	B	<0.0003
183. Lucky Mc mine	marcasite-pyrite	B	<0.0003
184. Lucky Mc mine	pyrite	O	0.41
185. Lucky Mc mine	pyrite-marcasite	O	0.10
186. Sarcophagus Butte	pyrite	B	0.002
187. Ridge No. 1 mine	marcasite (pyrite)	O	0.011
188. Ridge No. 1 mine	pyrite-marcasite	B	0.0008
189. Big Horn No. 18 claim	pyrite	B	0.003
Wasatch Formation (Eocene)			
Pumpkin Buttes dist., Campbell Co., Wyo.			
190. Channel claim	pyrite	O	0.01
191. Van No. 1 claim	pyrite	O	0.17
192. Craney Draw	pyrite (marcasite)	B	0.008
193. Craney Draw	pyrite (marcasite)	B	0.003
194. Jeanette mine	pyrite (marcasite)	O	0.03
195. Willow Creek	pyrite	B	0.004
196. Blowout mine	pyrite	O	3.00
Converse Co. dist., Wyoming			
197. Dead Cow area	pyrite	B	0.003
198. Fetterman Creek	pyrite	B	0.001
199. Dry Fork	pyrite	B	0.0003

TABLE 3—*Continued*

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
Crooks Gap dist., Fremont Co., Wyoming			
200. Helen May claim	pyrite	O	0.019
201. Sno Ball No. 1 mine	pyrite	O	0.005
Jackson Formation (Eocene)			
Karnes Co. dist., Texas			
202. Pete Lyssy claim	pyrite-marcasite	B	0.024
Browns Park Formation (Miocene?)			
Maybell dist., Moffat Co., Colorado			
203. Sugarloaf Mining property	pyrite-marcasite	O	0.006

[1] General geographic location of samples shown in Figure 1.
[2] X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.
[3] Sulfides divided into two types: O = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.
[4] Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample was available the lower limit of detection is correspondingly higher.

selenium, but only a few samples from any one formation were analyzed (Table 4). The average selenium content of 19 samples of pyrite or marcasite or both from these rocks is 0.0058 percent Se. Six sulfides from uranium ore average 0.005 percent Se, and 13 sulfides from barren rock average 0.006 percent Se. As these samples are so widely spaced and from several different formations, it is not possible to evaluate the relationship of the selenium content in the sulfides from barren rock as compared with the sulfides from ore-bearing rock.

The five samples of pyrite and marcasite from the Mancos shale of Cretaceous age were taken from a drill core located in the Slick Rock district, Colo., and these average 0.014 percent selenium. Trelease and Beath (32) have shown that the Mancos shale supports a variety of selenium-bearing plants (and it may be that the Se is derived from the oxidized iron sulfides). The sulfides in the Mancos occurred in a black shale containing no uranium minerals.

Sulfides from Hydrothermal and Igneous Rocks.—Various sulfide samples from hydrothermal deposits and intrusive rocks from the Colorado Plateau have also been tested for selenium to determine its spatial distribution with respect to the host rock and its mode of formation (Table 5).

Seven copper and iron sulfides from the laccolithic intrusions within the Colorado Plateau (including the La Sal, Utes, and Carrizo intrusives) average 0.008 percent selenium. Chalcopyrite from a diorite porphyry located in the La Sal Mountains, Utah, shows the maximum concentration of 0.016 percent Se. These contents, although much lower than many of those found in sulfides from sedimentary rocks, indicate the presence of selenium in the magmas giving rise to the intrusive rocks.

TABLE 4

SELENIUM CONTENT OF SULFIDES FROM SEDIMENTARY ROCKS OF CRETACEOUS AGE

Location[1]	Mineral[2]	Type[3]	Percent Se[4]
Fall River Sandstone			
Edgemont dist., Fall River Co., S. Dak.			
204. Flint Hill Quadrangle, sec. 23, T.8 S., R.3 E.	pyrite	B	0.0007
205. No. 4 mine	pyrite	O	0.006
206. Trail Fraction claim	pyrite	O	0.004
207. Flint Hill Quadrangle, sec. 15, T.9 S., R.4 E.	pyrite	B	0.0008
Crook Co. dist., Wyoming			
208. Busfield mine	pyrite	O	0.0006
209. Busfield mine	"pyrite"	B	<0.0003
210. Homestake mine	"pyrite"	O	0.017
Fuson Shale			
Edgemont dist., Fall River Co., S. Dak.			
211. Edgemont N. E. Quadrangle, sec. 35, T.7 S., R.2 E.	pyrite	B	0.001
212. Disney uranium mine	pyrite	B	0.008
Minnewaste Limestone			
Edgemont dist., Fall River Co., S. Dak.			
213. Burdock Quadrangle, sec. 8, T.7 S., R.22 E.	pyrite (marcasite)	B	0.002
Lakota Sandstone			
Crook Co. dist., Wyoming			
214. Shannon Oil Company claims	pyrite	O	0.0006
215. Shannon Oil Company claims	pyrite	B	0.0006
216. Shannon Oil Company claims	pyrite	O	<0.0003
Timpas Formation			
El Paso Co., Colorado			
217. Sec. 12, R.66 E., T.16 S.	marcasite	B	0.0007
Mancos Shale			
Slick Rock dist., San Miguel Co., Colorado			
218. Drill core, Disappointment Valley (depth 219.3 ft)	pyrite	B	0.023
219. Drill core, Disappointment Valley (depth 240.2 ft)	pyrite (marcasite)	B	0.028
220. Drill core, Disappointment Valley (depth 274 ft)	pyrite	B	0.003
221. Drill core, Disappointment Valley (depth 330.6 ft)	pyrite	B	0.008
222. Drill core, Disappointment Valley (depth 415.8 ft)	pyrite (marcasite)	B	0.007

[1] General geographic location of samples shown in Figure 1.

[2] X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

[3] Sulfides divided into two types: O = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

[4] Lower limit of detection is 0.003 percent Se for a 1-gram sample; when less sample was available the lower limit of detection is correspondingly higher.

TABLE 5

SELENIUM CONTENT OF SULFIDES FROM HYDROTHERMAL VEIN DEPOSITS AND INTRUSIVE ROCKS

Location[1]	Mineral[2]	Percent Se[3]
Intrusive Rocks		
La Sal Mountains, Grand Co., Utah		
223. Diorite porphyry	chalcopyrite	0.016
224. Contact zone in Paradox formation	pyrite	0.008
225. Diorite porphyry	pyrite	0.006
226. Diorite porphyry	bornite	0.015
Ute Mountains, Montezuma Co., Colorado		
227. Hornfels (Mancos shale) contact zone	pyrite	0.004
228. Diorite porphyry	pyrite	0.004
Carrizo Mountains, Apache Co., Arizona		
229. Diorite porphyry	pyrite	<0.001
Hydrothermal Vein Deposits		
Placerville dist., Montrose Co., Colorado		
230. Black King mine	pyrite	0.017
Rico dist., Montezuma Co., Colorado		
231. St. Louis Tunnel	pyrite	0.006
La Plata Mountains, La Plata Co., Colorado		
232. Bessie G. mine	pyrite	0.002
Monticello dist., Abajo Mountains, San Juan Co., Utah		
233. Blanding water tunnel	pyrite	0.010

[1] General geographic location of samples shown in Figure 1.
[2] X-ray identification on analyzed material; all samples taken from nonuraniferous rocks.
[3] Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample was available the lower limit of detection is correspondingly higher.

Four samples of pyrite from hydrothermal base-metal vein deposits of this region contain as much as 0.017 percent selenium, suggesting that selenium was present in the base-metal ore-forming fluids. Further testing is necessary to establish the regional and local trends in the sulfides from the hydrothermal deposits and the igneous rocks, but it seems that the Colorado Plateau area is a selenium-rich province.

MECHANISM OF SUBSTITUTION, SELENIUM FOR SULFUR

The mineragraphic study on these selenium-bearing sulfides has shown that inclusions of selenides within the sulfides are generally lacking, except for the clausthalite found in the chalcocites from Slick Rock district (Figs. 10, 11). Therefore, it is assumed that fluids from which these sulfides were deposited contained selenium, and that this selenium has entered the sulfur positions in the sulfide structure during crystallization.

The bonding in sulfides is generally considered to be a combination of covalent, metallic, and ionic. Both the atomic and ionic radii of sulfur and selenium are similar.

	Ionic radius (A)		
	Valence	Radius	Covalent radius (A)
Selenium	−2	1.98	1.17
Sulfur	−2	1.84	1.04

Goldschmidt's generalization (18) on isomorphous substitution shows that where ionic radii of two elements are within 15 per cent of each other the possibility of substitution is good. Both the ionic and covalent radii of S and Se fall well within the limit suggested by Goldschmidt. Other factors that may influence the isomorphous substitution, such as coordination number, polarization, and ionic potential are also similar in sulfur and selenium. Therefore, one may conclude, on the basis of crystal chemistry, that diadochic substitution of sulfur by selenium may be accomplished with comparative ease.

The pyrite containing large amounts of selenium (greater than 1 percent) shows some expansion of the lattice as might be expected, as selenium is somewhat larger than sulfur. Synthetic $FeSe_2$ has a structure similar to that of rammelsbergite (Gunnar Kullerud, personal communication) and it would seem that a complete solid solution between FeS_2-$FeSe_2$ is not possible on the basis of crystal chemistry. The temperatures and pressures of formation of the uranium ore deposits from the Colorado Plateau have been estimated to be less than 138° C and 800 atmospheres (11) and from this present study it appears that 3 percent by weight of selenium is the maximum amount that may enter the pyrite structure at these P-T conditions where excess Se is available. Ferroselite ($FeSe_2$) has been found associated with selenian pyrite; therefore where the sulfur and selenium are present in a reducing environment with Fe, about 4 percent (molecular) $FeSe_2$ can enter the pyrite (FeS_2) structure; and if excess iron and selenium are present, ferroselite ($FeSe_2$) is formed. This relationship seems to hold for the sulfide-selenide formation in the low temperature and pressure environment of the western uranium deposits, but at higher temperatures and pressures a complete FeS_2-$FeSe_2$ series with the pyrite structure might be possible.

The ferroselite ($FeSe_2$) from the AEC No. 8 mine, Temple Mountain, Utah, has a ratio of Fe : Co = 4 : 1 and here the structure is identical with that of $FeSe_2$ and also hastite ($CoSe_2$) described by Ramdohr and Schmitt (26). Thus a complete isomorphous series between $FeSe_2$-$CoSe_2$ seems to be possible.

Galena forms a complete isomorphous series between clausthalite as shown by Earley's work (14) on synthesis of this series. Most of the series was found to form under natural conditions at the Rifle mine, Colorado, where the galena-clausthalite band contains various proportions of Se in solid solution with S. These varying ratios of S and Se were reflected by an increase in the unit-cell size with an increase of Se as pointed out by Earley.

Bergenfelt (4) has shown that selenium apparently is enriched preferentially in different sulfides from the same mines. He has listed the sulfides in decreasing amounts of contained selenium: galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite. Edwards and Carlos (15) show that the

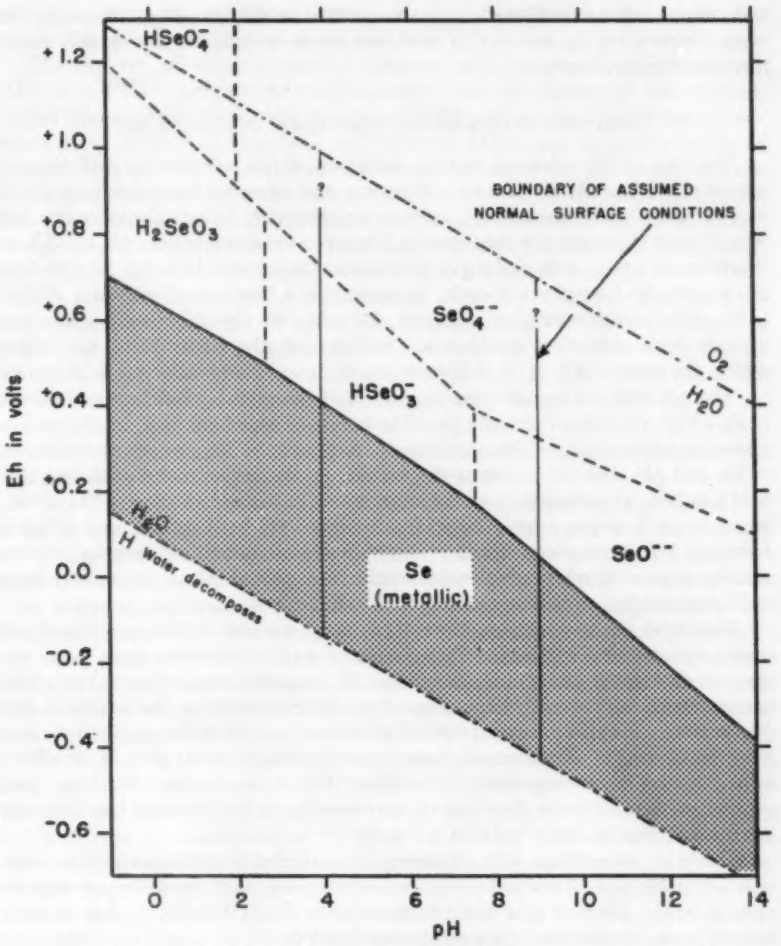


FIG. 15. Stability field of selenium (temperature 25° C, pressure 1 atm, concentration of Se 10^{-6} M)—after Delahay, Pourbaix, and Van Rysselberghe (12).

Australian sulfides have a completely different sequence, listed here in decreasing amounts of contained selenium: chalcopyrite, arsenopyrite, pyrite (hydrothermal), pyrrhotite, sphalerite, and galena.

As shown earlier, the S and Se atomic and ionic radii are similar and variations in size are probably slight from one sulfide structure to the next. It would seem that the amount of selenium available, crystal structure, and P-T conditions all control the amount of selenium found in any particular sulfide

from any one mine or district. This is verified in this investigation where the main controls on the amount of selenium found in sulfides are crystal structure and selenium supply.

OXIDATION OF SELENIFEROUS SULFIDES AND SELENIDES

The fate of the selenium during oxidation of the seleniferous sulfides and selenides is incompletely known. Selenites and selenates have not been found near oxidized selenium-bearing sulfides or selenides, but native selenium has been identified from many localities by Thompson and coworkers (31). These observations agree with the physical-chemical differences between Se and S in the geochemical weathering cycle, as pointed out by Goldschmidt and Hefter (19), who have shown that selenates and selenites are stable only under extremely high oxidizing conditions. Sulfates on the other hand are stable under the normal Eh-pH conditions found in oxidizing sulfide ore deposits.

The pH and Eh equilibrium diagram as presented by Delahay and others (12) (Fig. 15) illustrates the possible forms of selenium that might be expected under normal surface conditions. Krauskopf (24) has shown the limits of Eh and pH that are found at the surface under normal conditions and this field has been superimposed on the diagram. The diagram shows that metallic selenium is stable over a large area of this field both in acid and alkaline solutions. Selenites may form at high oxidation potentials, particularly in alkaline solutions, whereas selenates might be expected only in extremely high oxidizing conditions as suggested by Goldschmidt.

The field observations support these assumptions, which are based on thermodynamic calculations. Two forms of native selenium have been observed: the stable hexagonal form, and an unstable monoclinic form. The native selenium commonly crystallizes near or implanted on the oxidized sulfide grains. Pinkish crusts composed mostly of soluble sulfates contain intergrowths of native selenium and these crusts form near mine portals or where mine waters have evaporated. Selenium has been detected in mine and ground waters, although the form of the selenium in these waters has not been established, that is, SeO_3^{--}, $HSeO_3^-$, or SeO_4^{--}.

Limonitic concretions formed during oxidation of seleniferous sulfides contain selenium, and Byers and coworkers (6) believe that the selenium may be present in the limonite as a basic ferric selenite $Fe_2(OH)_4SeO_3$; this selenite has not been isolated from the seleniferous limonite.

DISCUSSION

Some of the rocks of Mesozoic and Tertiary age of the Colorado Plateau and Wyoming are rich in selenium, which is strongly concentrated in the sulfides formed before or during ore deposition. The presence of significant quantities of selenium in hydrothermal sulfides and in sulfides formed in the intrusive rocks of the region shows that this area is a selenium-rich province.

An adequate hypothesis regarding the sources of selenium concentrated in the sulfides should explain the differences in selenium content of the various

geologic formations, variations within a single formation, and the availability of selenium during deposition of the sulfides.

The average selenium content of igneous rocks as given by Goldschmidt (18) is 0.000009 percent Se; sedimentary rocks exclusive of the western United States generally contain less than 0.0001 percent Se. Selenium is concentrated in sulfides of magmatic and volcanic origin and in native sulfur of volcanic origin. Also, selenium can be concentrated in sediments derived from seleniferous source rock, such as that recorded in recent sediments in the Gulf of California (25). Therefore, three possible sources of selenium should be considered: selenium derived from volcanic activity, selenium from magmatic fluids, and selenium from pre-existing seleniferous terrains.

The selenium in the Morrison formation seems to have been derived from both volcanic emanations and reworked volcanic debris. Waters and Granger (33) have shown that volcanic materials are common in the Morrison, and as the sulfides from barren and mineralized rock in the Morrison contain the same relative amounts of selenium it seems likely that the selenium was introduced into the Morrison during its deposition by attendant volcanism. No evidence was found to support the idea that the source material for the Morrison other than the volcanics was seleniferous.

The Chinle formation of Triassic age also contain volcanic debris (33), and this seems to be the source of the Se in these rocks, but either the primary volcanic source for this material must have contained less selenium than the primary volcanic source of the Morrison debris or the over-all volume of volcanic material was much less. The Temple Mountain deposits present a different picture as there is a strong enrichment of selenium in the sulfides from ore when compared to the barren sulfides. The source of the selenium here seems to be hydrothermal fluids (23) whose magmatic source may have been rich in selenium, or the selenium may have been abstracted from seleniferous beds through which the hydrothermal solutions passed.

The source of the selenium within the sulfides from the sediments of Tertiary age in Wyoming is apparently tuff beds. Selenium-bearing tuffs in the Wind River Basin, Wyoming, have been described by Beath and others (3) and they report a maximum of 187 ppm Se. These tuffs are either incorporated in or overlie the Wind River formation. The enrichment of Se in the sulfides from coarse arkosic uraniferous sandstone when compared to the sulfides in nonuraniferous mudstones illustrates the fact that the selenium has been introduced into the Wind River formation by downward or laterally percolating ground water charged with selenium derived from these tuffs. The seleniferous sulfides were concentrated at or near the top of the ground-water table, whereas the sulfides in barren rock below the ground-water table were protected by impervious mudstones and show negligible selenium. The uranium follows the same depositional pattern as the selenium, and it would seem to have an origin related to that of the selenium; hence, the uranium and selenium are geochemically coherent in the Wind River formation.

The presence of selenium in the base-metal hydrothermal ores from the Colorado Plateau region indicates that deposits produced by hydrothermal fluids may have derived their selenium from igneous intrusions enriched in

selenium, or these fluids may have abstracted selenium from seleniferous beds through which they passed.

The ultimate source of the selenium in the sulfides from the Colorado Plateau and Wyoming can be related to a magmatic province that has contained exceptionally high selenium during periods of volcanic and intrusive activity in Mesozoic and Tertiary times.

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THE SYNTHESIS AND PROBABLE GEOLOGIC SIGNIFICANCE OF MELNIKOVITE

HENRY LEPP

ABSTRACT

The aged precipitate formed by the action of hydrogen sulfide on dilute alkaline ferrous solutions at room temperature has properties nearly identical to those recorded for the discredited mineral melnikovite. This precipitate gives a distinctive X-ray powder pattern, suggesting that melnikovite may be a valid mineral species. Final proof of species validity awaits actual comparison of the natural and synthetic material. In view of the marked similarity the precipitate has tentatively been named synthetic melnikovite.

Synthetic melnikovite is a sooty black, cryptocrystalline, magnetic, iron sulfide or sulfide hydrate. It changes to pyrite when subjected to temperatures above 75° C. Synthetic melnikovite is readily soluble in dilute hydrochloric acid and it reacts with carbonated water at room temperature to form ferrous bicarbonate.

The solution of melnikovite by carbonated water may be an intermediate step in the formation of sedimentary iron minerals. Melnikovite and related unstable iron sulfides have possibly played significant roles in the formation of sedimentary iron deposits.

INTRODUCTION

MELNIKOVITE and hydrotroilite have not been considered mineral species for many years. This is not surprising for hydrotroilite because it was never studied mineralogically and its species validity has always been questioned. The physical and chemical properties of melnikovite, however, were determined by Doss (6, 7) who reported it to be an amorphous, black, magnetic iron sulfide that was soluble in cold dilute HCl.

Doss' work, unfortunately, was carried out before the development of X-ray techniques for mineral analysis. He assumed from its texture and on the basis of chemical tests that melnikovite was amorphous. Subsequently a number of investigators (8, 11, 23, 25, 30) have X-rayed black, apparently amorphous iron sulfides only to find that they were either pyrite or marcasite. As a result melnikovite is now considered a variety of pyrite or marcasite as indicated by the names melnikovite-pyrite, melnikovite-marcasite and gelpyrite. Doss (7) pointed out that melnikovite was inherently unstable and that it changed to pyrite in time. Consequently, more recent X-ray analyses of similar materials have not actually discredited his mineral because the material studied may originally have been melnikovite. This possibility is strengthened by the fact that all X-ray studies have been made on non-magnetic material.

In the course of the present study an iron sulfide with essentially the same physical and chemical properties as melnikovite was prepared in several ways. Although positive proof of correspondence between the natural and synthetic

material is lacking because melnikovite specimens were not available for comparison, the marked similarity seems to justify use of the name synthetic melnikovite for the precipitated material. Certainly synthetic melnikovite has properties that distinguish it from the common sulfides pyrite, marcasite, or pyrrhotite. It is hoped that this study will renew interest in the black iron sulfides and thus uncover naturally occurring examples.

PREVIOUS SYNTHESES

Although knowledge of melnikovite as a mineral is incomplete, its habitat and mode of formation are fairly well understood. Sedimentary melnikovite, pyrite, or pyrrhotite found in black shales have formed by the action of H_2S or the sulfide ion on ferric or ferrous salts under slightly alkaline conditions, i.e., in the euxinic environment. Doss (7) considered the Black Sea bottom as the typical area for the formation of melnikovite. Consequently, although there have been no direct attempts to synthesize melnikovite; studies of the precipitates formed under the above conditions are pertinent to this investigation.

Before X-rays were used, Allen et al. (1) studied the reactions between iron and sulfur under various physical and chemical conditions. They found the black precipitate formed by the action of H_2S on ferrous salts in slightly alkaline solutions to be a mixture of ferrous sulfide and sulfur. This precipitate changed to pyrite on heating with excess polysulfide. Concerning the products of these experiments they (1, p. 184) concluded:

> Evidently they are not pure pyrite, a result somewhat surprising in view of the previous work; for if we obtain marcasite from more acid solutions, marcasite with pyrite from practically neutral solutions, we should naturally expect pure pyrite from alkaline solutions. Further investigation has led us to believe that the products of the alkaline solutions do not contain marcasite, but are mixed with amorphous disulfide.

Allen's work on the mineral sulfides of iron was repeated by Lundquist (20) who used X-ray methods to identify his products. Although this more recent work confirms the original study insofar as outlining the conditions for pyrite and/or marcasite formation, there is no mention of an amorphous sulfide or of melnikovite. Possibly Lundquist's experiments were continued too long at the 100° C plus temperatures thus causing any melnikovite which might have formed to convert to a more stable iron sulfide.

Alsen (2, 3), in his determination of the crystal structure of pyrrhotite and pyrrhotite-type minerals prepared synthetic pyrrhotite by heating freshly precipitated iron sulfides to high temperatures in H_2S. Pyrite was formed from the same precipitates when they were exposed to H_2S at moderate temperatures. Unfortunately Alsen did not record crystallographic data for the freshly precipitated sulfide, but he remarked (3, p. 24):

> The powder photographs show the crystal structure of the precipitated sulfide to be completely different before than after heating. Probably the untreated precipitate is a hydrate of FeS. A similar structure is formed when an intimate mixture of iron and sulfur powders are wet with a little water.

Michel and Chaudron (21) challenged Alsen's statement concerning the structure of the precipitate formed by the action of H_2S on slightly alkaline ferrous solutions. They dried similar precipitates in a stream of hydrogen at 150° C and obtained pyrrhotite. In view of the marked affinity of hydrogen for sulfur it is not surprising that Alsen's results were not duplicated.

The preceding syntheses have all involved reactions between ferrous solutions and H_2S or the sulfide ion. Theoretically one would expect the products of these reactions to be iron monosulfides, but in practice there is commonly an excess of sulfur over the 1:1 ratio. Studies of the reaction between ferric iron and H_2S also show that sulfur is usually more abundant than is indicated by the equations:

$$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O$$
$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

The additional sulfur probably results from the interaction of H_2S and extraneous oxygen. Lipin (18) was able to synthesize a compound of composition Fe_2S_3 by bubbling H_2S through a suspension of Fe_2S_3 only when great care was taken to insure the complete absence of air.

With the exception of the melnikovite described herein, the existence of distinct structural types of iron sulfides other than the common disulfides and monosulfide has not been established. Several unusual iron sulfides such as Fe_2S_3 and Fe_3S_4 are described in the chemical literature, but in every case crystallographic data are lacking, so a positive comparison with synthetic melnikovite is not possible. The iron to sulfur ratio of synthetic melnikovite was not determined by analysis. Tests indicated that it was near but less than 1:2. Doss (7) reported the melnikovite from Samara, Russia to have the formula Fe_8S_7.

The main difficulty encountered in comparing and identifying these unusual iron sulfides lies in their instability. Griffith and Morcom (12) reported that the sulfide formed by the interaction of H_2S and any form of iron oxide or hydroxide (Fe_2S_3) begins to break down at temperatures over 20° C to form a mixture of FeS_2 (pyrite) and a highly magnetic sulfide Fe_8S_9 (pyrrhotite). Pearson and Robinson (24) and also Lipin (18) similarly described the breakdown of Fe_2S_3 into FeS_2 and FeS.

Experimental work with iron sulfide precipitates seems to support the idea that there are other natural iron sulfides or sulfide hydrates than those commonly recognized. In fact there is reason to believe that several different, relatively unstable, black iron sulfides or sulfide hydrates exist. These studies strengthen the case for melnikovite.

SYNTHESIS OF MELNIKOVITE

In a first attempt iron sulfide was precipitated by adding NH_4HS to a dilute solution of $FeSO_4.7H_2O$. The very fine grained, jet black precipitate thus formed took several days to settle completely, after which it was washed a number of times by decantation with warm, recently boiled water. The pre-

cipitate was finally separated by a super centrifuge. It was dried in a dessicator filled with CO_2.

The dried product was a brittle, dense, sooty-black material which broke with a conchoidal fracture. It was easily attracted by even a weak hand magnet. The material was soluble in dilute HCl with the evolution of H_2S. It gave a distinctive X-ray powder pattern, the data for which are recorded in Table 1.

TABLE 1

X-RAY POWDER DATA OF SYNTHETIC MELNIKOVITE
Unfiltered Fe Radiation, Radius of Camera = 57.3 mm.)

No.	d° A	I*
1	3.80	2
2	3.45	2
3	3.27 beta	2
4	2.96	9
5	2.71 beta	1
6	2.46	9
7	2.09	1
8	2.01	1
9	1.92 beta	3
10	1.89	4
11	1.83	1
12	1.739	10
13	1.561	1
14	1.507	1
15	1.420	2
16	1.283	1
17	1.231	1
18	1.140	1
19	1.102	2
20	1.007	6

* Relative intensities with strongest line given an intensity of 10.

A small amount of light buff alteration was formed on the sharp edges of the dried iron sulfide precipitate during the drying process. This was determined to be pyrite with minor goethite; suggesting that the precipitate may alter to pyrite. Since melnikovite is also said to convert to pyrite, and to be black, magnetic, and soluble in dilute HCl, it seemed not unreasonable to assume that the present sulfide is synthetic melnikovite.

The synthetic melnikovite gave off water in a closed tube, and an attempt was therefore made to determine the quantity and nature of the water present. A small amount of coarsely powdered melnikovite was heated to near constant weight in an open crucible at various temperatures as recorded in Table 2. The mineral lost weight at temperatures up to 150° C after which it commenced to gain in weight; suggesting that the water present is loosely combined, probably in part water of hydration. The gain in weight after 150° C was due to oxidation.

Lokka (19) made similar studies on a natural hydrous iron sulfide which resembled melnikovite, but which was nonmagnetic and insoluble in dilute HCl. He found a 7.9 percent weight loss at 100° C with a gradual weight increase at higher temperatures. It is noteworthy, in the case of synthetic melnikovite, that almost all the magnetism was lost after heating at 200° C.

The product after the final heating at 250° C was a mixture of pyrite and hematite.

During the preparation of melnikovite, whenever the iron sulfide precipitate was oxidized in water before filtering, the product was gamma-$Fe_2O_3.H_2O$. On the other hand, alpha-$Fe_2O_3.H_2O$ was formed when the separated synthetic melnikovite was oxidized at room temperatures during the drying process. A similar observation had previously been made by Griffith and Morcom (12). They found that at temperatures below 50° C, alpha-$Fe_2O_3.H_2O$ formed when sulfides were oxidized in moist air, whereas gamma-$Fe_2O_3.H_2O$ formed when the oxidation took place in aqueous suspension.

TABLE 2

THE DEHYDRATION OF SYNTHETIC MELNIKOVITE

Temp., ° C	Weight, grams	Difference from original weight in %	Remarks
52	0.1914	0.0	No change
105	0.1798	− 6.1	No change
150	0.1696	−11.4	No change
200	0.1712	−10.6	Lost magnetism
250	0.1752	− 8.5	Brownish cast

Synthetic melnikovite was subsequently made a number of times from dilute ferrous solutions, either by adding NH_4HS, or by bubbling H_2S through the solution made alkaline (pH 8–9) with NaOH or NH_4OH. The very fine initial precipitate in each case was not attracted even by a strong magnet. In one of the syntheses it was noted that the fine, colloidal-like, initial precipitate began to settle from the bottom upwards. After three days the bottom half of the Erlenmeyer flask had completely cleared while the top half still contained the colloidal precipitate. At this time the bottom of the flask was covered with a thin layer of melnikovite. This suggests that melnikovite is not the first product formed, that it is due to some secondary reaction or to recrystallization.

EXPERIMENTS WITH MELNIKOVITE

The following tests were made to determine the nature and stability of synthetic melnikovite.

Expt. 1—A small quantity of synthetic melnikovite was sealed in a pyrex tube with a solution of NH_4HS. After 24 hours of heating at 200° C the material was completely altered to pyrite.

Expt. 2—A 0.2 gram sample of powdered synthetic melnikovite was heated in a tube furnace for 1 hour at 135° C in a stream of CO_2. No alteration was detectable in the X-ray powder photograph of the product.

Expt. 3—Synthetic melnikovite was placed in a cylinder used for making polished section briquettes. The material was held at a temperature of approximately 75° C and a pressure of 14,000 psi for one hour. Scattered

bright, brassy yellow grains of pyrite were visible in the product with a binocular microscope and an X-ray powder photograph showed a strong pyrite pattern with only the two strongest melnikovite lines.

Expt. 4—This experiment was made to determine the solubility of melnikovite in carbonated water. Melnikovite was prepared in the usual manner and the precipitate was washed by decantation with recently boiled distilled water over a period of four days, until the water showed no ferrous iron test and no hydrogen sulfide odor. Carbon dioxide was then bubbled through the water containing the melnikovite for a period of about 24 hours. The liquid was subsequently separated by filtration. This filtrate showed a pH of 4.5 and exhibited a strong odor of H_2S. After filtration the melnikovite was again placed in a flask with distilled water and the process was repeated. After 24 hours exposure to the carbonated water the remaining precipitate was once more separated by filtration. In both cases the filtrates showed strong ferrous iron tests. On standing in open beakers each developed an appreciable amount of a light-colored precipitate which soon became yellow-brown in color. The reactions are probably as follows:

$$FeS_x + 2H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2S + (x - 1)S$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + H_2O + CO_2$$

$$2FeCO_3 + 3H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3 + 2CO_2$$

These experiments corroborate Doss' original work on melnikovite in demonstrating that it is relatively unstable, and that it may be a transitory phase in the development of pyrite or other sulfides. Melnikovite, therefore, should only be found in geologically recent deposits.

Experiment 4 showed that melnikovite is soluble in carbonated water. Kauko and Haulio (15) previously demonstrated that ferrous sulfide (FeS) dissolves in carbonated water as $Fe(HCO_3)_2$ which is precipitated as $FeCO_3$ upon escape of CO_2. In many ways melnikovite behaves like iron monosulfide. Both may be magnetic, and both are soluble in dilute HCl and H_2CO_3. Melnikovite must have a higher iron to sulfur ratio than 1:1 because it may be largely altered to pyrite (Expt. 3) without addition of external sulfur.

The results of Experiment 3 cannot, however, be interpreted as showing a 1:2 iron to sulfur ratio for melnikovite. Small quantities of newly formed pyrrhotite (to 20%) are difficult to detect in pyrite by X-ray (8, 26). Ehrenberg (8) found only pyrite lines in an X-ray powder photograph of a black sulfide corresponding to $13FeS:87FeS_2$ in composition. He was able to identify the pyrrhotite microscopically after heating.

The obvious answer to determining the iron-sulfur ratio in melnikovite is chemical analysis. This presented a problem also because the material in question was too fine grained for purification by physical means. The synthetic melnikovite always contained small quantities of admixed oxides, and there is reason to believe that some very fine, uncombined sulfur may have been present.

THE ROLE OF MELNIKOVITE IN THE FORMATION OF SEDIMENTARY IRON DEPOSITS

Krumbein and Garrels (17) and Huber and Garrels (14) have stressed the importance of pH and redox potential in the formation of sedimentary iron deposits. In their experiments these investigators used dilute ferrous solutions to demonstrate that iron carbonates, oxides and sulfides were the products of distinctive combinations of pH and Eh. They supposed a similar situation to exist in nature.

The manner in which the iron of large sedimentary deposits was transported is still open to question. Regardless of manner of transport, ferrous solutions are required, for example, in the formation of siderite. Borchert (5) proposed that weathering solutions as such must have been relatively unimportant in the formation of sedimentary marine iron deposits. He suggested that the ferrous solutions required for the formation of these deposits were probably generated in the sea itself, in what he called the "Kohlensaure-Zone"; a zone believed to occur beneath the surface layer of oxygenated water. Here decaying organic matter generated soluble $Fe(HCO_3)_2$ from insoluble iron minerals (largely oxides). The iron solutions thus formed would be moved by ocean currents and precipitated as oxides, carbonates, sulfides or silicates depending upon the prevailing chemical conditions on the ocean floor.

Melnikovite and other black, unstable iron sulfides are known to form to a greater or lesser degree in ocean, lagoon, or lake bottoms. These iron sulfides are associated with black shales high in carbonaceous matter. Since melnikovite is soluble in carbonated water, and since it may well be the first product of the reduction of ferric iron by H_2S, it may represent an important intermediate stage in the formation of other iron minerals.

Before lithification, carbonaceous areas on the ocean floor may have been rich in fine-grained, black iron sulfides; unstable compounds very sensitive to changes in chemical environment. If, during a transgression of the sea, such a sulfide area were removed from the zone of active accumulation of organic matter and instead exposed to carbonated deoxygentated water, much of the sulfide might be dissolved. The resulting solutions could deposit a variety of iron minerals depending upon the physico-chemical conditions existing at the sites of deposition.

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MINERALOGY OF LIMONITE IN LEAD–ZINC GOSSANS[1]

WILLIAM C. KELLY

ABSTRACT

Differential thermal analysis was applied to 112 specimens of gossan limonite obtained from cappings over lead-zinc ores of highly varied geologic setting and primary mineralogy. It was hoped that variations in the proportions of lepidocrocite and goethite in gossan limonite would show a dependency on the type or grade of original ore or on the degree of transportation of the iron oxides.

Rather than revealing new outcrop criteria of value in the search for ore, this study showed that differential thermal analysis cannot, as formerly thought, be used for reliable identification of the hydrous ferric oxide minerals.

No lepidocrocite was found in any of the gossan specimens analyzed; the predominance of goethite in leached lead-zinc outcrops is explained in terms of the conditions under which the two minerals, goethite and lepidocrocite, are synthesized in the laboratory.

An application of thermal analysis to study of hematite-goethite-jarosite assemblages in oxidized copper ore outcrops is suggested.

INTRODUCTION

THE term "limonite" is accepted today as referring to any natural aggregate of unidentified hydrous ferric oxides lacking apparent crystallization (14, p. 105). Posnjak and Merwin (15) proved for the first time that goethite and lepidocrocite are the only valid members of what was formerly thought to be the "limonite series" of hydrates of ferric oxide. These two minerals have the same chemical composition ($Fe_2O_3 \cdot H_2O$) but differ in the nature of their hydrogen-oxygen bonding (6). In 1944, Blanchard (1) demonstrated the variable composition of impure substances commonly grouped under the heading of limonite by chemical analysis of twenty gossan specimens. To date, however, there has been no extensive study of variation in the occurrence of the two limonite minerals in lead-zinc gossans, mainly because of the difficulties involved in their identification by optical means.

When, in 1951, Kulp and Trites (13) stated that goethite and lepidocrocite could be identified by differential thermal analysis, the identification of these minerals in many gossan samples seemed practicable for the first time. After an application of this technique to nearly 100 samples of natural hydrous ferric oxide, these writers concluded that:

> "The thermal curves of goethite and lepidocrocite are sufficiently different to permit semi-quantitative estimation of these minerals in natural mixtures. The common occurrence of lepidocrocite in most aggregates of natural hydrous ferric oxide (limonite) is surprising."

[1] Publication authorized by the New Mexico Bureau of Mines and Mineral Resources.

The standard thermal analyses for goethite, lepidocrocite, and goethite-lepidocrocite mixtures are shown in Figure 1. These are typical curves from the original publication by Kulp and Trites.

These writers suggested a possible application of their technique to hydrous ferric oxides in leached ore outcrops:

"Differential thermal analysis appears applicable to a systematic study of gossans, since both goethite and lepidocrocite may be estimated semi-quantitatively. Systematic variations in the hydrous iron oxide minerals with the position of an ore body or with the type of ore mineral present might be expected. Such variations would certainly reflect changing geochemical conditions."

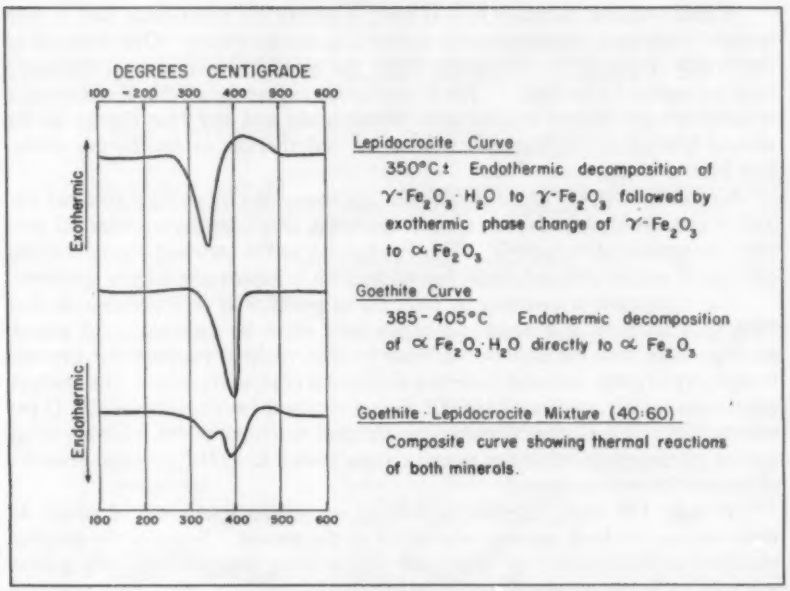
DEGREES CENTIGRADE
100 200 300 400 500 600
Exothermic
Endothermic
100 200 300 400 500 600
Lepidocrocite Curve
350°C ± Endothermic decomposition of γ-Fe2O3·H2O to γ-Fe2O3 followed by exothermic phase change of γ-Fe2O3 to α Fe2O3
Goethite Curve
385-405°C Endothermic decomposition of α Fe2O3·H2O directly to α Fe2O3
Goethite-Lepidocrocite Mixture (40:60)
Composite curve showing thermal reactions of both minerals.

FIG. 1. Standard differential thermal curves of the natural hydrous ferric oxides (after Kulp and Trites, 1951).

Following this suggestion, the present writer applied differential thermal analysis to many samples of gossan limonite collected in different mining localities where a close correlation between primary ore and leached outcrop could be established. Hydrous ferric oxides derived from very different primary sulfide sources were tested in the hope that variations in their thermal curves could be related to differences in their hypogene sources. Some specimens closely resembling the type limonites with "key structures" described by Blanchard and Boswell (1 to 5) were analyzed to determine whether this technique would be useful in identifying limonites of similar derivation but lacking these recognizable features. In addition, a number of thermal

analyses were made to detect any goethite-lepidocrocite variations that might aid in the distinction of indigenous and transported limonites as described by previous workers in this field (2, 14).

EQUIPMENT AND PROCEDURE

The apparatus used in the thermal analysis of gossan limonites was the same equipment used by Kulp and Trites in establishing the standard curves for the hydrous ferric oxides. This equipment has been described by Kulp and Kerr (12), and a theoretical treatment of differential thermal analysis is presented by Spiel et al. (17).

A dual-terminal thermocouple is used to record the addition or loss of heat in the sample as its temperature is raised at a constant rate. One terminal of the couple is placed in the sample while the other is inserted in a thermally inert substance (alundum). The temperature difference of this thermocouple is automatically plotted against oven temperature and any heat change in the sample appears in the thermal curve as an endothermic or exothermic deviation from a straight base line.

Approximately 0.5 gram of limonite are consumed in a single thermal run and, if randomly picked from a hand specimen, this quantity of material provides a representative sample. This is affirmed by the constant reproducibility of thermal curves obtained for different samples from any given hand specimen.

The equipment is sensitive to amounts of goethite or lepidocrocite of over 10% in a mixture and lesser quantities may often be detected. All gossan samples were powdered (dry) at least to 200 mesh to produce the greatest uniformity of grain size and therefore maximum peak sharpness. The thermal runs were usually continued to 600° C at a constant heating rate of 12° C per minute. At 600° C, the characteristic thermal reactions of the hydrous ferric oxides are complete, but some samples were heated to 1,000° C if the presence of impurities was suspected.

All told, 159 analyses were performed on gossan specimens of which 47 were repeats to check the reproducibility of the curves. Some of the original standard samples tested by Kulp and Trites were interspersed with gossan analyses to assure standard conditions.

RESULTS OF THERMAL ANALYSES OF GOSSAN LIMONITES

Thermal curves typical of those obtained from gossan limonites derived from different primary sources are presented in Figure 2 and the samples are described in Table 1. Comparisons of these curves with the standard thermal analyses for goethite and lepidocrocite left considerable doubt as to the true identity of the iron oxides present in the outcrop samples. The fact that no double endothermic peaks were obtained in any of the curves at least seemed to rule out the occurrence of goethite-lepidocrocite mixtures. However, many of the curves corresponded to standard lepidocrocite analyses while others had the shape of goethite curves but with the endothermic reaction appearing at lepidocrocite temperatures.

TABLE 1

GOSSAN LIMONITE SAMPLES TESTED BY THERMAL ANALYSIS

Thermal curve	Locality	Description
1	Providencia Mine, Zacatecas, Mexico	Limonite forming boxworks after sphalerite. Primary ore-vertical chimneys of high-grade lead-zinc ore in limestone. Pyrite high in ore and locally dominant sulfide. Gangue—both carbonates and quartz.
2	Capete Mine, Sonora, Mexico	Indigenous limonite from gossan over cupriferous pyrite veins. Cubic voids. Sample picked from voids and adjacent areas.
3	Grant County Mine, Hanover, New Mexico	Limonite from pyrite gossan. Cubic voids. Gangue (thuringite) thoroughly altered to goethite. Original material-pyrite in chloritized shale.
4	Pewabic Mine, Hanover, New Mexico	Limonite from pyrite gossan. Original material-cubic pyrite in completely chloritized granodiorite dike. Gangue weathers to limonite at surface.
5	Grecian Bend Ore Body, New Mayberry Mine, Bingham, Utah	Limonite from capping directly over auriferous pyrite replacement ores in quartzite.
6	Hobo Vein, Bullfrog Mine, Vanadium, New Mexico	Limonite from pyrite gossan. Cubic voids. Original material-pyrite disseminated in chloritized granodiorite.
7	Elizabeth Mine, Strafford, Vermont	Limonite from thin (2–5′) capping over pyrite-chalcopyrite-pyrrhotite ore in phlogopite-tremolite-carbonate rock.
8	Milan Mine, New Hampshire	Limonite in capping over pyrite-chalcopyrite lenses in schist. Gangue—chiefly quartz, some cordierite.
9	Anita Mine, New Mexico	Siliceous limonite forming ridges in boxwork after sphalerite. Original ore about 4% Zn, 6% Pb, 0.5% Cu, low pyrite. Lead-zinc veins in basalt and granodiorite. Gangue chiefly quartz.
10	Bullfrog Mine, Vanadium, New Mexico	Siliceous limonite forming ridges in leached sphalerite cavities. Primary ore—5–25% Zn, 0.5–1.0% Pb, low Cu. Pyrite low to moderate in ore. Gangue chiefly quartz and granodiorite fragments.
11	Grant County Mine, Hanover, New Mexico	Coatings of limonite and hematite in gossan voids after marmatite. Some siliceous impurities. Primary ore—marmatite in chloritized shale. Massive marmatite with little pyrite. No copper or lead.
12	Shingle Canyon Mine, New Mexico	Limonite from poorly developed sphalerite boxworks in siliceous gossan. Negligible pyrite and galena in primary ore. No copper. Gangue chiefly silica and kaolin.
13	Hidden Treasure Mine, Ophir Hill Area, Utah	Limonite forming ridges in well-formed boxworks after galena and sphalerite. Primary ore—galena dominant, sphalerite locally dominant, low copper, low pyrite. Gangue chiefly carbonates.

TABLE 1—*Continued*

Thermal curve	Locality	Description
14	New Mayberry Mine, Bingham, Utah	Limonite in capping over lead replacement body in limestone. Much relict galena in outcrop. Primary ore—galena dominant, minor pyrite, no copper. Gangue chiefly quartz.
15	Pewabic Mine, Hanover, New Mexico	Limonite in cavities after sphalerite. Sample also contained limonite after gangue (salite). Primary ore—sphalerite in pyrometasomatic silicates (ilvaite, salite, hedenbergite). Minor pyrrhotite in ore.
16	Lark Vein, Bingham, Utah	Limonite forming boxworks after galena and sphalerite. Primary ore—lead-zinc veins in limestone and quartzite. Galena dominant, sphalerite, small quantities of pyrite and chalcopyrite. Gangue of quartz, clays, country rock fragments.

X-ray powder patterns were obtained for 35 of the samples tested thermally and, without exception, these proved to be goethite patterns. No lepidocrocite lines were seen in any of the X-ray films. The writer has previously discussed the apparent anomalies in the thermal curves of gossan limonites (10), but it might be said in summary that the goethite from gossan samples is so poorly crystallized that it decomposes well below the reaction temperatures of the well-crystallized goethite samples tested by Kulp and Trites. Viewed under the electron microscope, the gossan goethites (Fig. 3) showed only slight evidences of crystallization even at very high magnifications whereas all of the standard goethites were very well crystallized (Fig. 4). Although the gossan limonites gave definite goethite X-ray powder patterns, the lines were broad and in many films the known lines of lesser intensity were indistinct or missing. When tested on the X-ray diffractometer, the goethites used by Kulp and Trites in their work gave sharp peaks high above background whereas the gossan goethites gave broad, indistinct reflections.

When poorly crystallized gossan goethite was mixed with well-crystallized goethite and both ground to a uniform *particle size* (200 mesh), thermal analyses of the resulting mixtures frequently matched the standard curves for goethite-lepidocrocite mixtures.

These results were of mineralogic interest in showing that the standard differential thermal curves for goethite, for lepidocrocite, and for goethite-lepidocrocite mixtures can be produced by goethite alone—the variations depending upon the degree of crystallization in the materials analyzed. However, from the standpoint of the gossan study, the results were negative in that they revealed no new outcrop guides of value in the search for ore.

The thermal curves of gossan limonites were surprisingly uniform and showed no variation with the grade, gangue, or country rocks of the original ores. The only primary feature that seemed to affect the limonite formed in the gossan was the relative abundance of original pyrite. Goethite after pyrite alone or after lead-zinc ores very high in pyrite produced thermal curves with marked exothermic reactions following the endothermic peaks (Fig. 2, Curves

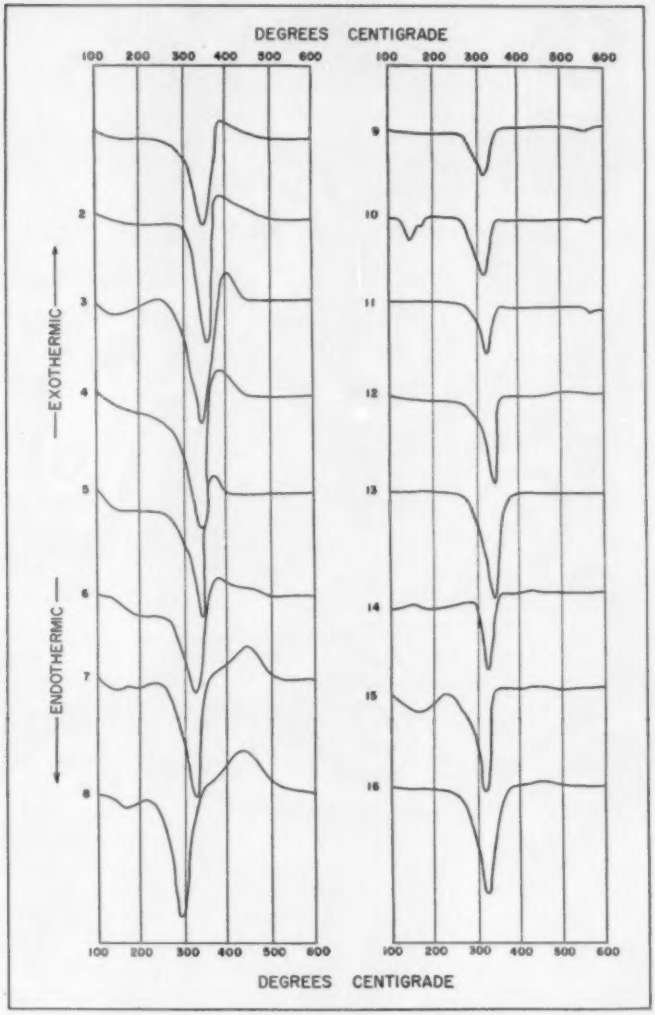

FIG. 2. Differential thermal curves of gossan limonites.

1–8). Similar curves were obtained from goethite pseudomorphs (poorly crystallized) after pyrite. The exothermic peaks were not present in the thermal curves of goethite after lead-zinc ores of low to moderate pyrite content (Fig. 2, Curves 9–16).

The practical significance of this difference in the curves is questionable because the exothermic reactions vary independently of the actual quantities of pyrite in the primary sulfide source. They merely appear where pyrite has been abundant, but provide no quantitative measure of that abundance. Furthermore, exothermic peaks also appeared in thermal curves of the few limonites of chalcopyrite and magnetite derivation that were tested; therefore this reaction is not an exclusive indicator of pyrite as distinct from these other minerals in the primary iron source.

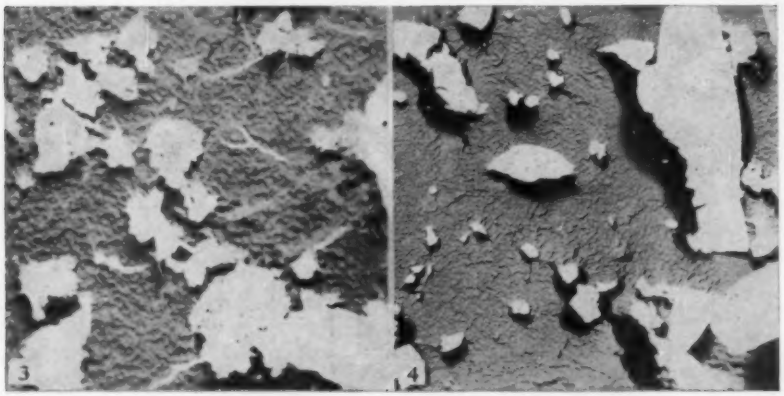

FIG. 3. Electron photomicrograph of goethite from pyrite gossan at the Pewabic Mine, Hanover, New Mexico. This poorly crystallized goethite decomposes at 350° C and gives a thermal curve typical of limonite derivatives of pyrite. (× 13,000.)

FIG. 4. Electron photomicrograph of well-crystallized goethite from Tavistock, Devonshire. This material decomposes at 400° C and produces a standard goethite thermal curve such as that shown in Figure 1. (× 13,000.)

As yet, no satisfactory explanation can be given for the erratic appearance of the exothermic peaks in these gossan goethite curves. X-ray analyses of the heated products chilled at the peaks of endothermic decomposition produced gamma-Fe_2O_3 (maghemite) patterns when an exothermic peak had appeared in the goethite curve and alpha-Fe_2O_3 (hematite) patterns when the exothermic peak was absent, indicating that the exothermic reaction was a phase change of gamma- to alpha-Fe_2O_3. This phase change is generally associated with lepidocrocite, but these gossan limonites are all goethite. The conversion of gamma- to alpha-Fe_2O_3 does not appear in the thermal curves of well-crystallized goethite because it is very rapid above 400° C, and the loss of heat is supposed to be too fast to register on the thermal apparatus. Since the poorly crystallized gossan goethites decompose well below this temperature, the phase change might be expected to appear in their thermal curves. The lower decomposition temperatures would not explain, however, the absence of this reaction in curves of limonites derived from low-pyrite sources. Small amounts of water vapor might catalyze the phase change (8), but those

limonites that produced the exothermic reaction probably contained more uncombined water than those that did not. This is indicated by the low-temperature endothermic drift in Curves 1 to 8, Figure 2. An additional feature, difficult to explain, is the fact that the exothermic reactions in some of the high-pyrite derivative curves continued well above 400° C, past the point where the phase change is supposed to be instantaneous.

A number of samples of limonite of a clearly transported origin were analyzed for comparison with indigenous oxides in each of several districts studied. The transported oxides were characterized by laminated, botryoidal, or stalactitic structures. Again, no differences were noted in the thermal curves which would be of practical aid in drawing the significant distinction between these two types of limonite. X-ray studies of transported limonites again showed the absence of lepidocrocite and predominance of goethite.

PREDOMINANCE OF GOETHITE IN LEAD–ZINC GOSSANS

The predominance of goethite in lead-zinc gossan limonites is consistent with the experimental conditions under which the two limonite minerals have been synthetically prepared in the laboratory (9, 19). Goethite is formed by the slow hydrolysis of most ferric salts (the chloride excepted) or by the aging of the gel formed by the oxidation of ferrous compounds. On the other hand, lepidocrocite forms on oxidation of newly prepared, hydrous FeS, $2Fe_2O_3 \cdot 3FeO$, Fe_2S_3, and hydrous Fe_3O_4. It is also obtained on oxidation of ferrous chloride in the presence of sodium azide or pyridine at controlled pH conditions. It is apparent that the experimental conditions so far found favorable to the formation of goethite are more analogous to the natural conditions in the zone of oxidation. The known reagents used in the laboratory to form lepidocrocite would be absent, whereas the gels derived from ferrous compounds and solutions of ferric salts, especially the sulfate, would be common in oxide zone.

In a study of the system Fe_2O_3–SO_3–H_2O, Posnjak and Merwin (16) found that goethite is formed by hydrolysis of dilute ferric sulfate solutions at temperatures below 130° C. They obtained no lepidocrocite from this system which is, at present, our best approximation to the natural environment for iron in the oxide zone.

POSSIBLE APPLICATION OF THERMAL ANALYSIS TO COPPER GOSSANS

Although the application of differential thermal analysis to lead-zinc gossan limonites brought out little in the way of new criteria for the prediction of hidden ores at depth, it would seem that an application of this technique to leached copper ore outcrops might bring a greater return in practical results. Tunell (18, 14, p. 105–107) has shown that the copper outcrops at Morenci, Bingham, and Tyrone contain hematite and jarosite as well as goethite, and that the ratios of these minerals are significant as guides to the type of original ore. Thermal analysis would provide a rapid means for an otherwise difficult determination of the proportions of these minerals in a gossan specimen.

Standard curves for the analysis of the mineral ratios in natural aggregates could be set up with artificial mixtures of known proportions. Jarosite has a very distinctive thermal curve with two prominent endothermic reactions at 460° C and 800° C (11). Since it has been shown here that gossan limonites decompose at temperatures well below 400° C due to their poor crystallization, there should be little interference between the thermal peaks of goethite and jarosite. Hematite could be estimated from its depressive effects on the peak amplitudes of the two other minerals. This approach would be especially applicable to iron cappings over the porphyry-copper type of ore.

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THE USE OF LEACHABLE URANIUM IN GEOCHEMICAL PROSPECTING ON THE COLORADO PLATEAU

I. THE DISTRIBUTION OF LEACHABLE URANIUM IN CORE SAMPLES ADJACENT TO THE HOMESTAKE ORE BODY, BIG INDIAN WASH, SAN JUAN COUNTY, UTAH

HEINRICH D. HOLLAND, BETTY RUTH CURTISS, GEORGE E. McGILL, AND JOHN A. PETERSEN

ABSTRACT

Data on the concentration of leachable uranium, total uranium, beta-gamma activity, alpha activity, and petrography are presented for core samples from the vicinity of the Homestake ore body, Big Indian Wash, San Juan County, Utah. It is shown that the leachable uranium content in such cores is generally highest in the vicinity of the Chinle-Cutler contact, and that the contours of leachable uranium for this horizon outline satisfactorily the Homestake ore body and an east-west trending belt of mineralization including the Homestake and the Standard-Caluranium ore bodies. This trend is defined more precisely by data on the leachable uranium concentration than by the beta-gamma activity of the samples studied, and it is concluded that leachable uranium analyses may serve as a useful tool in exploration for uranium ore.

INTRODUCTION

THE prospecting methods used most widely in the search for uranium ore are those that depend on the radioactivity of uranium and its daughter elements. With the advent of scintillation detectors it has become feasible to measure gamma activity rapidly and precisely in the field and to detect with assurance small changes in gamma activity in the terrain which is being explored. However this method of prospecting suffers from the limitation that the effect on the recorded gamma activity of the members of the thorium series, of potassium, of members of the uranium series other than uranium, and, in the case of surface exploration, of cosmic rays cannot be separated readily from the radiation from uranium itself. This is a handicap particularly in the interpretation of very small anomalies. It therefore seemed of interest to explore the possibility of using the uranium content of soils and rocks as a guide to ore. The distribution of uranium in soils and rocks has been the subject of much intensive study (1, 8), and it has been found that a portion of the uranium in earth materials is generally acid soluble. Since the acid soluble portion of the uranium present in soils and rocks presumably bears a closer relationship than the total uranium content to nearby uranium mineralization, this study has concentrated in the main on a study of the leachable uranium concentration (LU) in soils and rocks.

The results of this study have been divided into two parts, the first dealing with core samples, the second with surface samples. This paper presents

our results on core samples taken from the vicinity of the Homestake ore body in Big Indian Wash, San Juan County, Utah. A second paper will present the data on soil and surface rock samples from a number of areas on and adjacent to the Colorado Plateau.

THE GEOLOGIC SETTING OF THE HOMESTAKE ORE BODY

The Homestake mine is located on the west side of Big Indian Wash, about 40 miles southeast of Moab, Utah and approximately 3 miles north of the MiVida mine, which has been described by several authors (4, 7). Both mines lie to the west of the Lisbon Valley fault, a major structural feature trending roughly northwest-southeast along the crest of a salt anticline. Ore is found in the lowest member of the Triassic Chinle formation, which dips approximately 13° to the southwest. The Chinle rests unconformably on the Permian Cutler formation with a discordance of approximately 2°.

The Cutler formation consists entirely of red beds in Big Indian Wash. The lower half of the formation contains dull, brownish-red, medium to coarse-grained sandstones. Dull reddish mudstones, siltstones, thin white marls, and lenses of coarse grained arkosic sandstone comprise the upper half.

The Chinle of Big Indian Wash can likewise be divided conveniently into two parts. The lower Chinle is greenish gray in color and consists of lenses of sandy limestone, limy siltstone, mudstones with varying amounts of lime, and lime pebble conglomerate. This part of the formation is rather resistant to weathering and is exposed on a cliff that terminates the bench formed by the upper Chinle, which consists of red mudstones and siltstones, and some sandstone and conglomerate.

THE MINERALOGY AND PETROGRAPHY OF THE CORE SAMPLES

Cores from the vicinity of the Homestake Mine were made available through the courtesy of the Homestake Mining Company. The location of the drill core samples is shown in Figure 1. Most of the samples were taken from the lower Chinle and upper Cutler formations. One sample of each lithologic unit less than 5 feet thick, and samples at 5-foot intervals of units more than 5 feet thick, were taken for analysis. The samples were stored in steel or aluminum containers. In the laboratory the samples were split, one half crushed on a bucking board for uranium analysis and radioactivity measurements, the remainder kept for petrographic and alpha track plate studies.

The sediments were divided into four size and seven color categories on the basis of examination with the naked eye and under the binocular microscope. The definition of size and color groups and the distribution of the samples studied among the various categories are shown in Table 1. It can be seen that most of the samples are greenish or greyish and of siltstone or fine sandstone size. The ratio of light to dark colored samples reflects the ratio of the number of samples taken from the lower Chinle to that taken from the Cutler formation. Extremely fine-grained sediments are rare and clays are present only in very minor amounts even in the fine-grained samples as shown by X-ray diffraction studies.

Thin sections of a number of samples were studied. These showed that quartz, plagioclase, microcline, and in some horizons limestone pebbles constitute the majority of the detrital grains. Carbonized wood, chert, sulfides, barite, and micaceous minerals as well as the ore minerals were observed in minor amounts. Calcite is present in considerable amounts in most of the samples. It is the major cementing material and occurs both in a very finely divided state and as larger grains and veins that cut fine-grained calcite, the feldspars, and, to a very minor extent, quartz. The relationships exhibited by the various forms of calcite suggest that a part of the original calcite matrix was recrystallized after deposition. Calcite sometimes is seen to fill fractures in broken quartz grains. Since such breakage of quartz in place generally

TABLE 1

GRAIN-SIZE AND COLOR DISTRIBUTION IN CORE SAMPLES FROM THE VICINITY OF THE HOMESTAKE MINE, BIG INDIAN WASH, UTAH
(Horizons sampled: lower Chinle and upper Cutler; total number of samples: 239)

Size group	Color group							Total in each size group
	(1) White	(2) Gray	(3) Green	(4) Orange	(5) Purple	(6) Maroon	(7) Buff Brown	
I. Siltstone (less than ca. 1/32 mm)	0	17	51	6	4	1	9	88
II. Fine sandstone (ca. 1/32 to 1 mm)	16	35	15	9	3	4	6	88
III. Coarse sandstone (ca. 1 to 4 mm)	11	12	1	0	0	1	2	27
IV. Conglomerate (greater than ca. 4 mm, or rock fragments present)	1	27	6	1	0	0	1	36
Total in each color group	28	91	73	16	7	6	18	

does not take place until a load equivalent to at least 5,000 feet of overburden has accumulated (Professor John C. Maxwell, personal communication), and since such a thickness of sediments probably did not accumulate on the Chinle until Upper Cretaceous time, recrystallization of the calcite presumably accurred at that time or more recently. Some of the larger calcite crystals are themselves broken.

Thin sections covered with alpha sensitive stripping film by a method described by Stieff and Stern (9) showed that the alpha activity emanates predominantly from small, dark, highly radioactive areas. X-ray diffraction patterns of the dark material showed it ot be coffinite or a mixture of coffinite and uraninite, in agreement with previous studies of the mineralogy of the ores from Big Indian Wash (3, 7). In some cases the coffinite and uraninite were associated with black, non-radioactive material which has been identified tentatively as a hydrocarbon; in others the uranium minerals were in the vicinity of woody remains, sulfides, and recrystallized calcite.

Small, highly radioactive grains were found rather unexpectedly even in sediments with a uranium content comparable to that of sediments in non-

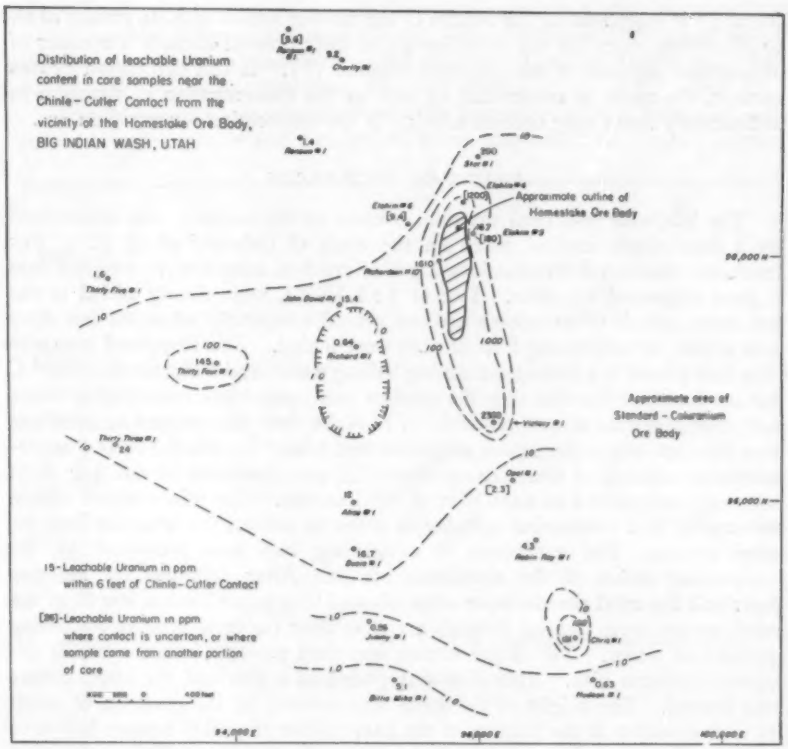
Distribution of leachable Uranium content in core samples near the Chinle–Cutler Contact from the vicinity of the Homestake Ore Body, BIG INDIAN WASH, UTAH
Approximate outline of Homestake Ore Body
Approximate area of Standard – Colorannium Ore Body
15–Leachable Uranium in ppm within 6 feet of Chinle–Cutler Contact
[36]–Leachable Uranium in ppm where contact is uncertain, or where sample came from another portion of core
90,000 N
94,000 N
94,000 E
98,000 E
400,000 E

FIG. 1.

mineralized areas. The pertinent data are shown in Table 2. This suggests that much of the uranium in the lower Chinle was either reconstituted even in areas which do not show an abnormally high uranium content, or that these grains are residual detrital material. That the latter alternative is probably

TABLE 2

DISTRIBUTION OF HIGHLY RADIOACTIVE GRAINS IN THIN SECTIONS OF CORE SAMPLES FROM THE VICINITY OF THE HOMESTAKE MINE

Sample no.	Leachable uranium	No. of highly radioactive grains per thin section
H-148	1,600 ppm	120
H-28	280	35
H-223	5.8	15
H-242	5.3	16
H-180	1.6	2
H-235	1.4	3
H-43	0.20	1

incorrect is suggested by the results of age studies which indicate an age of 60 to 70 million years for the ore minerals in their present form in a number of similar ore deposits of the Colorado Plateau (1). If this contention proves correct, the mode of occurrence as well as the concentration of uranium in sedimentary rocks may become a guide in the exploration for uranium ore.

ANALYTICAL TECHNIQUES

The leachable and total uranium content of the samples was determined by a fluorimetric method based on the work of Grimaldi et al. (2). For leachable uranium determinations 2 gm of crushed sample were weighed into a glass stoppered test tube. 5 cc of 1 : 1 HNO_3 were slowly added to the test tube, and, if effervescence had not ceased completely when the last drop was added, an additional 5 cc of acid were added. The stoppered test tube was then placed in a beaker containing boiling water, and maintained at 100° C for one hour. After this time the solution was poured into centrifuging tubes, and centrifuged for several minutes. 1 cc of the clear supernatant solution was then pipetted into a clean glass stoppered test tube. To this 8.5 cc of a supersaturated solution of aluminum nitrate (1.1 gm aluminum nitrate per cc of solution) were added as were 10 cc of ethyl acetate. The mixture was shaken thoroughly in a mechanical agitator in order to extract the uranium into the ethyl acetate. The extraction of interfering ions was prevented by the complexing action of the aluminum nitrate. After agitation the aqueous layer and the ethyl acetate layer were allowed to separate, and a few cc of the ethyl acetate were filtered through a coarse filter paper to remove remaining globules of water. 1 cc of the filtrate was then pipetted into a specially designed platinum dish. This dish was placed in a pan and the ethyl acetate was ignited. The height of the flame was reduced by the presence of about ¼ inch of water in the bottom of the pan. After the ethyl acetate had been burned off, the platinum dish was heated gently to drive off the remaining liquid, and 2 gm of flux consisting of a mixture of 45.5% Na_2CO_3, 45.5% K_2CO_3, and 9% NaF by weight were added to the residue. The mixture was heated over a burner until just liquid. The melt was agitated to ensure incorporation of all of the uranium and was then permitted to cool. The solidified melt was in the form of a button whose fluorescence was measured in a transmission type fluorimeter.

The fluorimeter was patterned after that developed by Grimaldi et al. (2). The housing was built by L. C. Eichner Instruments, Clifton, N. J., the power supply by F. Hamner, then of the Palmer Physical Laboratory of Princeton University.

The total uranium content of the samples was determined in a manner that differed only in the early stages from that described above. 0.5 gm of sample were mixed with 3.0 gm of Na_2CO_3 and fused gently in a platinum dish. Upon cooling, the residue was treated with 1 : 1 nitric acid, transferred to a 250 ml beaker, digested with an excess of water and 1 : 1 nitric acid and then taken to dryness. 10 cc of distilled water and 5 cc of 1 : 1 HNO_3 were added to the residue; the mixture was warmed, transferred to test tubes, and

centrifuged. 7.5 cc of the clear solution were added to a glass stoppered test tube containing 9.5 gm aluminum nitrate. The mixture was heated to disolve the aluminum nitrate, and then cooled slowly. 10 cc of ethyl acetate were added, and the mixture treated as described above.

The fluorimeter was standardized with buttons prepared from two solutions of uranyl nitrate and from subdilutions prepared from them. Aliquots

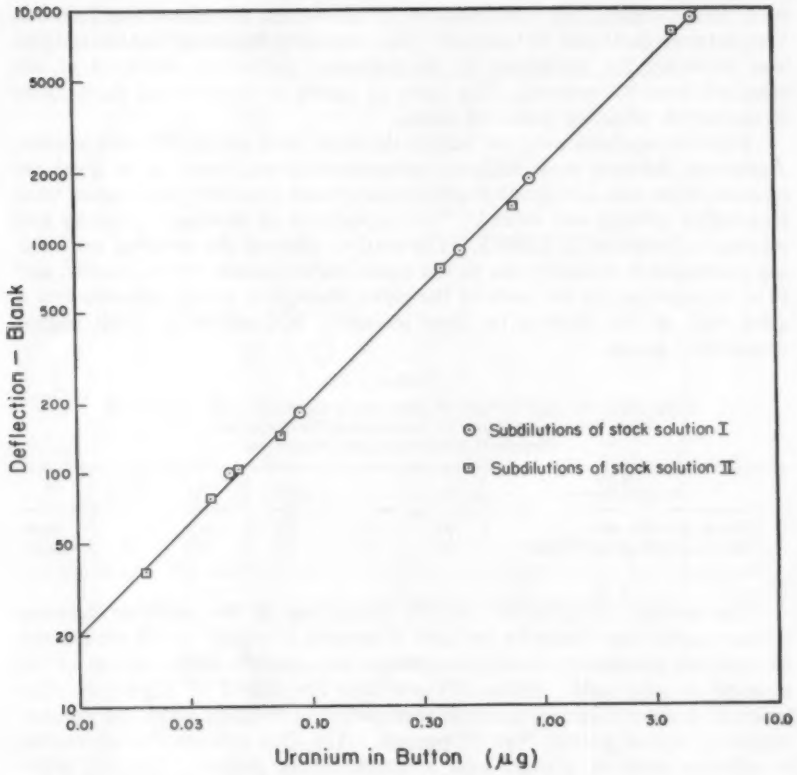

FIG. 2.

of slightly acidified uranyl nitrate solution were pipetted into the appropriate platinum dishes and evaporated to dryness. To the residue 2 gm of flux were added and buttons prepared as described above. The data relating the uranium content of buttons to the fluorescence intensity is shown in Figure 2. The relationship is linear in the concentration range studied.

Contamination of the samples was prevented as much as possible by cleaning all glass ware thoroughly with detergent. The platinum dishes were

soaked in nitric acid between fusions, and potassium pyrosulfate was fused in them frequently to remove any remaining traces of uranium.

Samples were analyzed in batches of ten. With each batch an aliquot of standard solution and a blank solution were run through. Frequently samples spiked with an aliquot of standard solution were analyzed to check on the relationship between the efficiency of the extraction procedure for pure uranyl nitrate solutions and for those containing a number of other ions extracted from rock samples. The efficiency of the extraction procedure was found to vary between ca 85 and 100 percent. The measured fluorscence of the samples was corrected for deviations of the measured extraction efficiency of the standard from 100 percent. The cause or causes of the observed fluctuations in extraction efficiency were not found.

Replicate analyses were run both in the same batch and in different batches. Agreement between such replicate measurements was found to be good for igneous rocks and adequate for sedimentary rocks provided the samples were thoroughly ground and mixed. The importance of thorough grinding and mixing is illustrated in Table 3. The marked effect of the grinding and mixing procedure is probably due to the considerable sample inhomogeneity, and is to be expected on the basis of the alpha track data which indicates that a good deal of the uranium in these sediments is localized in small, highly uraniferous grains.

TABLE 3

SOME DATA ON THE EFFECT OF THOROUGH GRINDING AND MIXING ON THE REPRODUCIBILITY OF LEACHABLE URANIUM ANALYSES
(Sample H-121; coarse gray sandstone)

Analysis no.	I	II	III	IV	V	VI
Coarse grinding only	48	101	56	28		ppm
Careful grinding and mixing	36	37	31	33	35	34 ppm

The strength of nitric acid in the initial step of the leachable uranium measurements was chosen on the basis of a series of tests in which the amount of uranium removed from a given sample was studied as a function of the strength of acid used. Some of the results are shown in Figure 3. The uranium extracted increases rapidly and becomes constant when the concentration of acid is greater than 30 percent. The data indicate that extraction is effective even in slightly acid solution. It is probable that the slight plateau in the data for sample H-49 is due to the higher calcite content of this sample. Apparently solution of the uranium is appreciable only in an acid medium, which is attained only after the solution of the carbonate present in the sample. Since no well defined break was observed in the curves of uranium extracted as a function of strength of acid, it was thought impracticable to attempt to distinguish between varieties of leachable uranium, i.e., between uranium present in different chemical combinations or in different physical environments in the samples studied. 1 : 1 HNO_3 was therefore used throughout in the analytical procedure in an attempt to reach for all samples studied the plateau as found for the three samples of Figure 3.

The alpha and beta-gamma activities of a number of samples were measured in an alpha scintillation counter and an end window geiger counter respectively. The alpha counter was of the type described by Kulp, Holland, and Volchok (6). The samples were crushed, and 11 gm weighed into a shallow dish. This was introduced into the counting chamber through a light-tight lock, and centered underneath an RCA 5819 photomultiplier tube whose photosensitive surface was coated with Patterson Type D ZnS phosphor. An Atomic Instrument Co. scaler and a Streeter Amet automatic register were used to record the counting data.

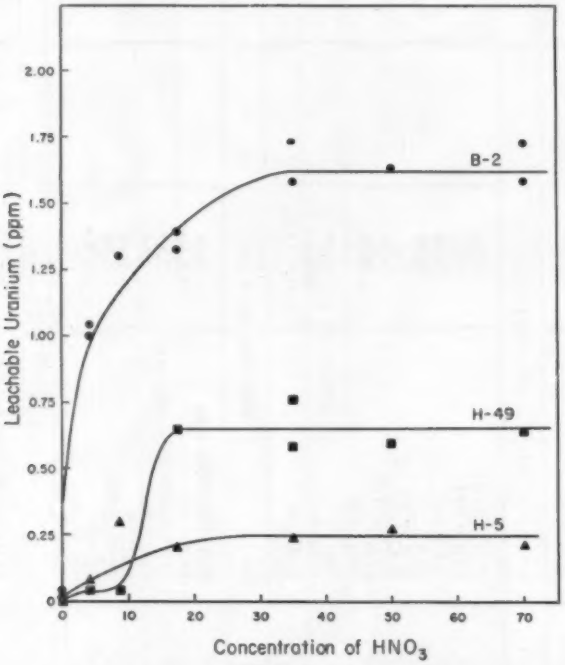

FIG. 3.

A D-34 Nuclear Instrument and Chemical Corporation end window geiger tube with a 1.4 mg/cm² mica end window was used to determine the beta-gamma activity of the samples. The tube was contained in a lead shield. Pulses were scaled and registered by means of a Nuclear Instrument and Chemical Corporation scaler. The background and sensitivity of the counters were checked frequently.

DISCUSSION OF RESULTS

The data on the location, lithology, uranium content, beta-gamma activity, and alpha activity obtained in this study are shown in Table 4. Samples are arranged by drill holes whose location is shown in Figure 1.

TABLE 4

COMPILATION OF DATA ON CORE SAMPLES TAKEN NEAR THE HOMESTAKE MINE, BIG INDIAN WASH, UTAH

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Alice No. 1				
H-115	643 ft	+ 33	IV(I)2,B(M)	0.36			
H-114	646	+ 30	IV(I)3,(M)	0.16			
H-113	647	+ 29	II2,M+Cl	0.23			
H-112	648.5	+ 27.5	I3,B	0.29			
H-111	649.5	+ 26.5	III2,W(C)	1.3			
H-110	656	+ 20	II(I)3,B+M	0.32			
H-109	663	+ 13	I3,O	0.53			
H-108	668	+ 8	IV(II)2,B	2.6			
H-107	669	+ 7	I3,B	0.99			
H-106	681	− 5	I5,M(B)	6.8, 6.1		13.6	
H-105	680.5	− 4.5	II(I)5,M	11.0, 13.5		11.4	
			Billie Mike No. 1				
H-56	740	+ 25	II(IV)2,Cl?+M+(S)	0.66			
H-55	740	+ 25	I2,B	1.7, 2.0			
H-54	745	+ 20	II(IV)2,B(W?)(M)(S)	1.1			
H-53	749.5	+ 15.5	IV(I)2,B	0.99			
H-52	749.5	+ 12	I(II)3,B	0.60			
H-51	759	+ 6	I7,(M)B	0.46			
H-50	769.5	− 4.5	III1,Cl	5.4, 4.8		6.9	
			Charity No. 1				
H-223	565	+ 5	IV(II)(I)2,W++S++(M)	5.5, 6.1			
H-222	567	+ 3	IV(I)(II)2,B	9.2, 9.5			
H-221	570	0	III,ClBS(C?)	7.8			
H-220	578.5	− 8.5	III1,Cl(B)(C?)	0.29			
H-219	582	− 12	III1,Cl(B)(C?)	0.26			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Charity No. 1 (*Continued*)				
H-218	587	− 17	II2,ClM	1.1			
H-216	592.5	− 22.5	II4,MCl	0.36			
H-217	598.5	− 28.5	II(I)4,Cl+M	0.26		6.8	
			Chris No. 1				
H-49	670.5	+ 0.5	III(II)2,Cl(B)	0.56			
H-48	671.	0	III1,O	106, 136	238	62.4	
H-47	675	− 4	II4,(B)	0.22			
H-46	691	− 20	II4,O	0.35			
H-45	697	− 26	II1,ClC	0.55			
			Elohim No. 1				
H-215	435	+ 41.5	I(II)(IV)3,O	0.82			
H-214	435.8	+ 40.7	II(IV)2,B(M)(S?)	15.2	15.7		
H-213	435.9	+ 40.6	II(IV)2,S++B	2.9			
H-212	437	+ 39.5	IV(II)2,W+BS	10.9	14.5		
H-211	444	+ 32.5	I3,B+	0.52			
H-210	451.5	+ 25	I(II)3,Cl(M)	7.8		15.5	
H-209	456	+ 20.5	II(IV)3,ClB+	2.5			
H-208	458.5	+ 18	II2,ClB(S)	180		61.5	
H-205	470.4	+ 6.1	II2,(Cl)(M)(B)	1.3			
H-206	471	+ 5.5	II2,M(Cl)	0.33			
H-204	472.5	+ 4	II(IV)2,S+	2.8			
H-207	473	+ 3.5	II(IV)3,M(Cl)(S)	0.37			
H-203	473	+ 3.5	III(II)2,(S)	16.7	35.4		
H-202	473.7	+ 2.8					
H-201	477	− 0.5	II5,Cl(B)	1.9			
H-200	493	− 16.5	II1,ClC	1.5			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Elohim No. 4				
H-134	440		III2,W?B?	21			
H-133	441		I(IV)3,BM	2.9			
H-132	441.5		IV(II)2,S	4.1			
H-131	444		I(II)3,B	1.0			
H-130	445.2		III2,W(S)	8.6			
H-129	446.8		I(II)2,B	10			
H-128	449		I3,(B)	0.44			
H-127	456		II(IV)3,(B)	0.43			
H-126	462		III1,C(Cl)(B)	0.69			
H-125	470.2		I3,B+M	3.6, 3.6			
H-124	474		I3,W(M)	3.0, 3.1	624†		
H-123	476		III1,O	630*	540	132.8	41.4
H-122	478		III1,O	1,250*	1,255, 1,169†	320, 309	113.0
H-121	481		III2,O	34		31.2	
H-120	493		II3,Cl	19			
H-119	495		III6,O	2.5			
H-117	503		II6,Cl+M	0.40			
H-118	504		II3,Cl+M	11			
H-116	515		II6,Cl+M	1.2			
			Elohim No. 6				
H-143	605	+ 65(?)	I3,MB(Cl)	1.4			
H-142	610	+ 60(?)	I3,(M?)	0.50			
H-141	610.5	+ 59.5(?)	II2,B	2.8			
H-140	611.5	+ 58.5(?)	I(II)3,B(W)(M)(S)	9.8, 8.9			
H-139	612.5	+ 57.5(?)	IV(I)2,(B)(Cl)	1.1			
H-138	615	+ 55(?)	I3,BM	0.88			
H-137	617	+ 53(?)	I3,WB(C?)	0.95			
H-136	648	+ 22(?)		0.48			
H-135	677	− 7(?)	II(III)6,B	0.16			

* Average of 12 determinations. † LU + RU.

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Hudson No. 1				
H-44	652	+ 24	I2(M)(B)	0.27		7.6	
H-43	657	+ 19	II2,WB+M	0.20		9.0	
H-42	659	+ 17	II1,BM(S)	1.2		4.3	
H-40	661	+ 15	II1,B(C)	1.4, 1.5		9.3	0.56
H-41	665	+ 11	I(II)2,O	0.95		3.9	
H-39	671	+ 5	I(II)7,O	0.22		7.8	
H-38	676	0	I3,O	0.63		6.9	
H-37	682	− 6	I4,M	0.75		6.2	
			Timmie No. 1				
H-67	742.5	+ 47.5	II(I)3,(M)(B)	0.16, 0.47			
H-68	752	+ 38	IV(I)2,W+M	2.6, 2.0, 2.1	5.8†		
H-66	760.5	+ 29.5	I3,MB(S)	0.24			
H-65	762	+ 28	IV2,S	1.5			
H-64	765	+ 25	I7,O	0.24			
H-63	770	+ 20	IV2,B+	1.4			
H-62	775	+ 15	I5,(B)	0.31			
H-61	778	+ 12	IV(III)7,O	0.55			
H-60	780.5	+ 9.5	I2,B	0.25			
H-59	785	+ 5	I3,B	0.34			
H-58	788	+ 2	I7,M	0.37			
H-57	794	− 4	I(II)6,MCl	0.56			
			John David No. 1				
H-172	600.5	+ 30.5	I2,(B)(M) & IV(II)2,B	6.8		3.9	1.07
H-171	601	+ 30	II2,B	0.98		1.6	0.46
H-170	602	+ 29	IV(II)3,(M)(B)	1.5, 1.4		3.7	0.87
H-169	611	+ 20	II2,(Cl)	0.81		2.1	0.48

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			John David No. 1 (*Continued*)				
H-168	614	+ 17	IV(II)2,WB	4.9, 4.6, 4.6		3.7	1.1
H-167	616.5	+ 14.5	I(II)3,B	0.43		8.2	1.0
H-164	622	+ 9	I(II)2,B + (M)	0.87		7.8	2.2
H-166	626	+ 5		4.1		9.7	1.9
H-165	627.5	+ 3.5	II(I)2,M(Cl)(B)	2.5		8.0	1.7
H-163	628.5	+ 2.5	II(I)(IV)7,Cl(B)	1.7		8.6	
H-162	630	+ 1	II(I)7,Cl + M(B)	14		11.4	2.9
H-161	631.3	− 0.3	II(III)7,B + C	15, 20	28†	11.0	3.7
H-160	631.5	− 0.5	II5,M	0.81		10.5	2.1
H-159	638	− 7	II(I)1,(M)(B)	0.94, 0.77		4.9	0.36
			Opal No. 1				
H-11	440.5	+ 56.5	IV(I)3,MClB	0.71		6.2	0.86
H-10	443	+ 54	II2,M + Cl(B)	1.2		3.1	0.52
H-9	447	+ 50	IV(III)(II)2,M(S?)	2.3			
H-8	450	+ 47	I3,M + (W)(B)	0.57, 0.32			
H-7	458	+ 39	IV(III)2,(B)	1.9, 2.4, 4.4	3.6, 3.4, 3.4		
H-6	462	+ 35	I3,B				
H-5	467	+ 30	I3,O				
H-4	472	+ 25	I3,B	0.50			
H-3	477	+ 20	I3,W	0.19			
H-2	482	+ 15	I3,M(Cl)(B)	0.22			
H-1	487	+ 10	I3,O?	0.33			
			Renown No. 1				
H-243	643		II2,(M)B + + S +	3.6			
H-241	647		I3,MB(W)(Cl)	0.31			
H-240	649		II2,MB(Cl)	1.7			
H-242	651		IV(II)2,WBS	5.3			
H-239	652.5		IV(II)2,B(S?)	5.1		2.5	
H-238	658		IV(II)2,B(S)	3.6			
H-237	661.5		IV(III)(II)2,B + (Cl)(M)	2.7			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Renown No. 1 (*Continued*)				
H-236	669		I2,B	0.39			
H-235	671		IV(I)2,B++	1.4			
H-244	674		17,(B)	0.31			
H-234	675			0.80			
H-233	678.4 (contact) (?)		II2,B(S?)	0.21			
H-232	680		I4(Cl)(M)	0.18			
			Renown No. 1. 1				
H-231	615.8		I2,B+(S)	0.73			
H-230	616		I3,(M)	0.35			
H-229	618		III(IV)2,(B)	1.9			
H-228	620		I3,WB(M)	0.35			
H-227	622		I2,(B)(M)	1.4			
H-226	625		IV(II)2,BS	5.6			
H-225	626.5 (contact) (?)		I3,Cl+M	0.85			
H-224	634		II4,Cl+M	0.26			
			Richard No. 1				
H-92	610	+ 21	I7,(B)	0.45			
H-91	615	+ 16	I7,(M)	0.30			
H-90	620	+ 11	I(II)3,O	0.51			
H-89	625	+ 6		0.80			
H-88	629	+ 2	II(I)6,M	0.64			
H-93	630	+ 1	III7,C	0.77			
H-87	637	− 6	III7,C(Cl)(B)	0.84			
H-86	656	− 25	I4,Cl+M+	0.27			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Richardson No. 10				
H-158	500	+ 60	II2,(C)(B)	0.91, 1.0			
H-157	515	+ 45	I3,B+	1.2			
H-156	520	+ 40	II2,(B)(C)	1.7			
H-155	521	+ 39	II2,(M)B	4.0			
H-154	522.8	+ 37.5	IV(II)(I)3,B+M	14			
H-153	536	+ 24	I(II)3,M(B)(C)	0.36			
H-151	541	+ 19	II(I)3,Cl,M	0.45			
H-152	543	+ 17	II3,ClMWB	5.4, 4.7		6.6	
H-150	551	+ 9	II(IV)3,ClBC	1.8			
H-149	552.5	+ 7.5	III(IV)1,C+B(M)	160, 108, 177		43.5	17.3
H-148	554	+ 6	III1,BC	1,610		603.3	
H-147	555.5	+ 4.5	III(IV)2,CM	47, 39, 37, 40		25.4	11.0
H-146	556.5	+ 3.5	I3,M	2.9			
H-145	559.5	+ 0.5	II(I)2,(M)	0.53			
H-144	563.5	− 3.5	I4,M	0.29			
			Robin Roy No. 1				
H-85	509	+ 32	IV(I)2,B	9.4		5.5	1.8
H-84	514	+ 27	II2,Cl+M+(B)	0.73			
H-83	525	+ 16	I3,O	0.64			
H-82	530	+ 11	I3,(B)	0.47			
H-81	535	+ 6	III1,(S?)	25	27	12.0	
H-80	536	+ 5	IV(III)(II)2,(B)(S)	1.2			
H-79	538	+ 3	I2,S(B)	0.27, 0.36			
H-78	544	− 3	I2,ClM+	4.3			
H-77	546	− 5	II(III)(I)2,M	3.9			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Star No. 1				
H-76	400	+ 22	II3,W+M	1.9			
H-75	403	+ 19		2.7			
H-74	409.5	+ 12.5	I3,O	1.1			
H-73	413	+ 9	III1,S(B)	9.0		5.9	
H-72	419	+ 3	I(IV)(II)3,B+	219, 165, 152, 192	206†	125.0	48.0, 45.4
H-71	421	+ 1	I3,B+	0.48			
H-70	425	− 3	I4,Cl+M+	1.2			
H-69	440	− 18	III1,Cl+(M)	0.25			
			Susie No. 1				
H-104	722	+ 29	II1,(Cl)(M)(B)	0.28			
H-102	722	+ 29	II1,MCl(C)	0.20			
H-103	726	+ 25	I(IV)2,B	0.35			
H-101	726	+ 25	I2,O	0.25			
H-100	731	+ 20					
H-99	733	+ 18	I3,O	0.33			
H-98	738	+ 13	I2,W++S+	1.0			
H-97	740	+ 11	I7,M	2.2			
H-96	745	+ 6	II(I)(IV)7,O	0.71			
H-95	749	+ 2	I3,M	0.55			
H-94	452	− 1	II7,(C)(M)	16.1, 16.5, 17.6		11.1	
			Thirty Three No. 1				
H-199	640.3	+103.2	IV(I)3,B	1.5			
H-198	645	+ 98.3	I(II)5,M	0.78			
H-197	657	+ 86.5	I(II)5,M	0.28			
H-196	658.3	+ 85.2	I3,B(M)	3.8			
H-195	659.5	+ 84.0	II(I)2,Cl(B)	0.27			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Thirty Three No. 1 (*Continued*)				
H-194	740	+ 3.5	II(IV)1,CB(M)	1.1			
H-193	741	+ 2.5	II(IV)2,MB	0.41			
H-192	743	+ 0.5	II(IV)(I)3,(M)	0.27		13.4	
H-191	744.5	− 1.0	II(III)1,B++C+	24			
H-190	759	− 15.5	II4,M	0.22			
			Thirty Four No. 1				
H-24	637	+ 62	II2,M+Cl+BW	0.08		2.8	0.44
H-23	654	+ 45	(IV(I)2,(M))?	1.6			
H-22	660	+ 39	IV(III)2,(S)M	1.9, 1.2		3.9	0.33
H-21	667	+ 32	II2,MB	0.96			
H-20	672	+ 27	I2,W+M	1.3			
H-19	677	+ 22	III1,C?	170, 110		40.7	21.4
H-18	682	+ 17	II2,MCl	1.6			
H-17	687	+ 12	II2,O?	4.8			
H-16	692	+ 7	III1,C?	120	122	33.3	14.0, 14.7
H-15	695.5	+ 3.5	III(2),(S)	151, 140	162	52.9	29.9, 30.5
H-14	696	+ 3	I4,M	0.50			
H-13	702.5	− 3.5	I3,Cl+(M)	1.7, 1.5		9.1	1.15
H-12	705	− 6	III1,(S)(C)	31	35	10.6	4.1
			Thirty Five No. 1				
H-189	690.5	+ 39.5	I3,(M?)	0.27			
H-188	698.5	+ 31.5	I(IV)2,W++S+B(M)	0.92			
H-187	701	+ 29	II3,(M)	0.25			
H-186	703	+ 27	II(IV)3,MClB	0.32			
H-185	707	+ 23	III(IV)2,(B)	2.1			
H-184	710.5	+ 19.5	I3,O	0.27			

TABLE 4 (*Continued*)

Sample no.	Depth in hole	Distance from Chinle-Cutler contact	Lithology	Leachable uranium content (ppm)	Total uranium content (ppm)	Gamma activity (counts per minute)	Alpha activity (counts per minute)
			Thirty Five No.1 (*Continued*)				
H-183	713.8	+ 16.2	III(IV)2,(S)	2.0			
H-182	718	+ 14.2	III(IV)3,S	5.5, 5.9	12.2	6.9	
H-181	721	+ 9	II2,B	1.2			
H-180	726	+ 4	IV(II)2,B+(M)	1.6			
H-179	728.2	+ 1.8	I3,BM	0.26			
H-178	729	+ 1		1.5			
H-177	730	0	II3,B(M)	0.74			
H-176	746.5	− 16.5	II4,Cl+(M)	0.14			
H-175	749	− 19	II1,B	0.30			
H-174	761	− 31	II4,MCl	0.16			
H-173	766	− 36	II4,MCl+	0.22			
			Victory No. 1				
H-36	535.5	+ 39.5	IV2,O	4.7, 4.5			
H-35	537	+ 38	I(IV?)2,(W)	7.5		4.2	1.2, 1.4
H-34	550	+ 25	I3,(B?)	1.2			
H-33	556	+ 19	I(IV?)7,O	0.21			
H-32	561	+ 14	I3,(M)(Cl)(B)	7.1, 8.8		7.4	
H-31	565	+ 10	IV(III)(I),C+	1.5			
H-30	565.5	+ 9.5	IV(III)2,C	28, 26, 36	36, 44	16.1	
H-29	568	+ 6.5	I3,W+(M)	2,300	3,700	774, 760	257, 234, 239
H-28	—	—	II(III)2,BM	280		102.0, 98.9	
H-27	575	0	II1,(Cl)(M)(C)	0.20			
H-26	581	− 6	III2,Cl+	0.11		7.3, 7.4	0.31, 0.27

Key to Table 4

Roman numerals: grain size classification as in Table 1.
Arabic numerals: color classification as in Table 1.

W. Carbonized wood.
C. Orange chert.
S. Sulfides.
M. Muscovite.
Cl. Chlorite.
B. Unidentified black grains (probably fragments of wood, uranium minerals, obsidian?, or murky calcite).
0. None of the above.

Abundances are estimated and recorded as in this example:

(W) Wood present, but only as rare fragments.
W Wood present and readily noticeable.
W+ Wood abundant.
W++ Wood extremely abundant.

The uranium content of the residue from the acid leaching treatment of a number of samples was measured in order to determine the relationship between leachable and total uranium content in these samples. The pertinent data, taken from Table 4, are reproduced in Table 5. Almost all of the uranium present in highly mineralized samples was found to be acid soluble, as was to be expected from experiments of uranium extraction from ores of this type. Approximately one half of the uranium in non-mineralized samples was found to be leachable, and this can probably be taken as a rough measure of the ratio of leachable to total uranium in the samples used in this study.

TABLE 5

THE RELATIONSHIP OF THE LEACHABLE AND TOTAL URANIUM CONTENT OF SOME CORE SAMPLES FROM THE VICINITY OF THE HOMESTAKE ORE BODY

Sample no.	Lithology	Leachable uranium	Uranium in residue	Total Uranium
H-122	Coarse white sandstone	1,165 ppm	4.0 ppm	1,169 ppm
H-123	Coarse white sandstone	620	4.3	624
H-72	Fine green siltstone	190	16	206
H-161	Fine buff-brown sandstone	20	8.0	28
H-222	Gray conglomerate	9.5	4.3	13.8
H-182	Coarse green sandstone	6.0	6.2	12.2
H-68	Gray conglomerate	2.6	3.2	5.8

Most of the samples were found to have a leachable uranium content of less than 2 ppm, and this figure can be taken as the approximate upper limit of the LU content of unmineralized samples. The remaining samples showed LU concentrations up to and exceeding 2000 ppm, the lower limit or ore grade material in this area. Both lithology and location of the samples were found to influence their LU content. Table 6 shows a breakdown of the LU content of the samples according to lithology. The percentage of samples in the three groups of LU content falls toward the right for all lithologies except the coarse sandstones, of which 45 percent were found to have LU concentrations in excess of 25 ppm.

TABLE 6

THE RELATIONSHIP OF LU CONTENT TO THE LITHOLOGY OF THE SAMPLES

Lithology		No. of samples in group	Percentage of samples with LU		
Group	Description		Less than 5 ppm	5 to 25 ppm	Greater than 25 ppm
I	Siltstone	88	91	7	2
II	Fine sandstone	88	85	13	2
III	Coarse sandstone	27	37	18	45
IV	Conglomerate	36	75	22	3

This observation clearly has a bearing on the evaluation of LU analyses in exploration and reflects a control for the deposition of uranium ore in this environment. Thin sections of a number of samples of coarse sandstone were

TABLE 7

THE LEACHABLE URANIUM CONTENT AND THE MINERALOGICAL COMPOSITION OF SOME COARSE SANDSTONE SAMPLES FROM THE VICINITY OF THE HOMESTAKE ORE BODY

Sample no.	LU (ppm)	Quartz	Limestone fragments	K-feldspar	Plagioclase	Green biotite	Muscovite	Tourmaline	Detrital chert	Zircon	Sericite (?)	Secondary calcite	Secondary barite	Sulfides	Undetermined opaques	Phosphates (?)	Chalcedony
H-26	0.11	25		25		20	—	—	—	—	30	<1	—	—	—	—	—
H-49	0.56	40	35	7	2	<1	<1	—	1	<1	—	15	—	—	—	—	—
H-93	0.77	50	20	8	2	—	<1	—	—	—	—	20	—	—	—	—	—
H-229	1.94	7	85	2	1	—	—	—	<1	—	—	5	—	—	—	—	<1
H-12	31	50	20	5	—	<1	—	—	—	—	—	25	—	<1	—	<1	—
H-48	106	35	40	10		—	—	—	—	—	—	10	5	—	—	—	—
H-16	120	40	20	8	2	<1	—	—	<1	<1	—	30	—	<1	—	—	—
H-15	151	40	15	12	2	—	—	—	—	—	—	10	20	—	<1	—	—
H-19	168	55	15	10	5	—	<1	<1	1	—	—	15	—	<1	—	—	—
H-148	1,610	55	20	3	2	—	<1	—	—	—	—	20	—	—	—	—	—

prepared, and approximate modal analyses were made in an effort to determine a correlation between the petrography of these samples and their LU content. The results are shown in Table 7 and are entirely negative. They suggest that the environment and/or the location of a given coarse sandstone rather than its lithology determines its LU content.

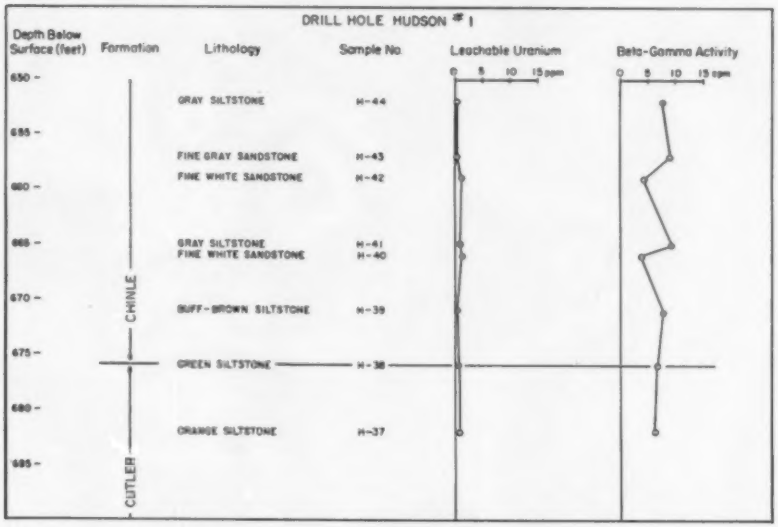

FIG. 4.

The effect of the location on the LU content of the samples can be subdivided into a vertical and a horizontal component. A study of Table 4 indicates that both components can exert a considerable effect. This is illustrated in Figures 4 and 5 which reproduce in graphical form the data for drill holes Hudson No. 1 and John David No. 1. The LU content of all samples in the former drill hole is less than 1.5 ppm, whereas the LU content of several samples in the latter hole exceeds 1.5 ppm by a considerable margin. The peak of LU concentration near the Chinle-Cutler contact is particularly pronounced. These two holes can probably be taken as representative of an unmineralized and slightly mineralized hole respectively. A maximum in the

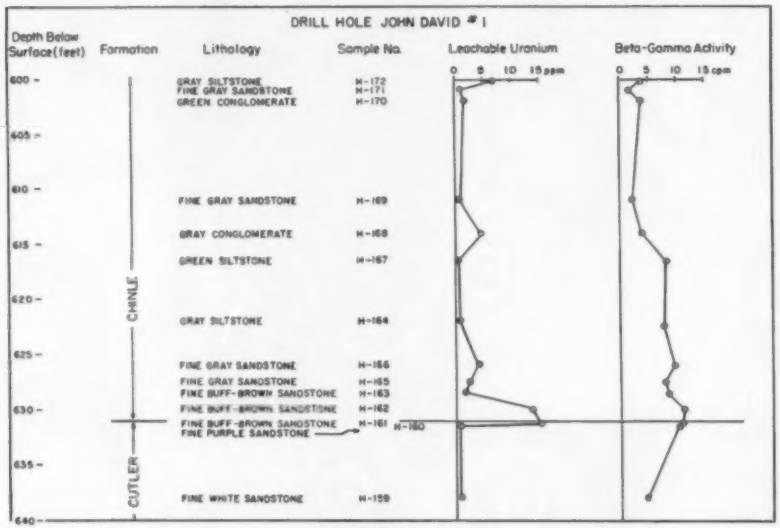

FIG. 5.

LU concentration at or near the Chinle-Cutler contact was observed in a number of other drill holes. This observation suggests that it may be permissible to restrict sampling to a zone straddling this contact in applying LU analysis data to exploration for uranium ore in this area.

The relationship to the Homestake ore body of maximum LU values in core samples taken from a zone extending 6 feet into both formations from the Chinle-Cutler contact is shown in Figure 1. Since the number of drill holes studied is relatively small, the contouring of LU values is not very satisfactory. However the decrease of LU content away from the Homestake ore body is clearly shown. Furthermore the presence of slightly mineralized ground west of this ore body is strongly indicated suggesting the presence of an east-west trend of mineralization in this area.

The value of delineating such a trend depends on the correlation of such a trend with ore; the feasibility of outlining such trends by means of LU

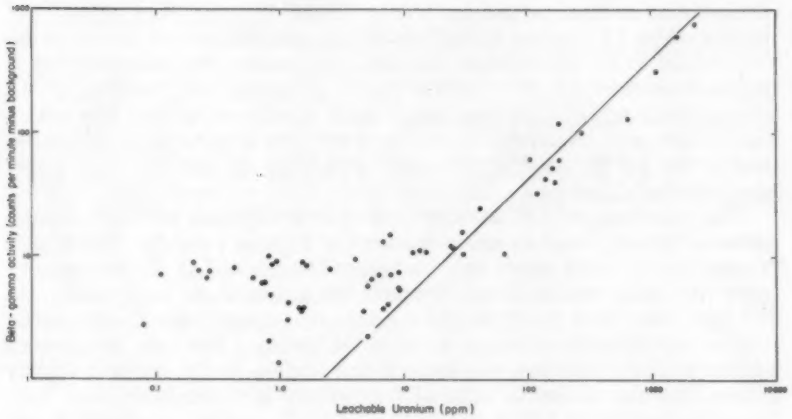

FIG. 6.

analyses depends on the relative cost and ease of this method. The importance of outlining such trends is difficult to evaluate definitively on the basis of the present data. However the relationship of the relative ease of outlining such a trend by means of LU analyses and by means of radiometric techniques can be determined with some certainty. Figure 6 is a plot of the beta-gamma activity of a number of samples against their LU content. When the LU concentration is above 20 ppm the two quantities are proportional, indicating that the beta-gamma activity of such samples is determined primarily by the

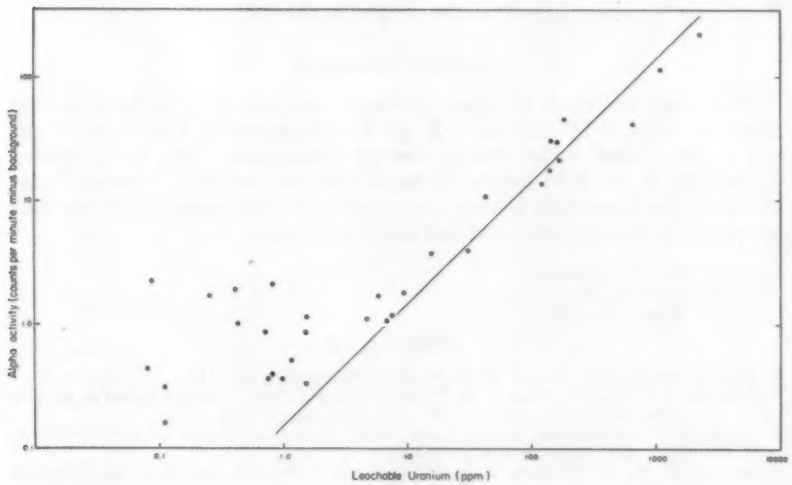

FIG. 7.

concentration of beta and gamma emitters in the uranium decay series. For samples whose LU content is less than 20 ppm the beta-gamma activity is not proportional to the LU content. In such samples the beta-gamma activity is largely determined by the concentration of potassium and members of the thorium decay series. Since for such samples there is no clearcut relationship between beta-gamma activity and LU content, anomalous uranium concentrations in this range cannot be determined with certainty with the usual geiger or scintillation detectors.

The superiority of LU analyses over total beta-gamma activity measurements in outlining small anomalies is shown in Figures 4 and 5. In drill hole Hudson No. 1, which shows only background values of LU, the beta-gamma count rate varies between 5 and 10 counts per minute above background. In drill hole John David No. 1 the LU concentration at the Chinle-Cutler contact rises to ten times its maximum value in the previous hole; the beta-gamma activity similarly rises to a maximum at this horizon, but is still only slightly greater than the maximum value of this activity in the unmineralized hole. Thus, if anomalies in LU in the range of 2 to 20 ppm are significant in exploration for uranium ore, their delineation can be made more definitively on the basis of LU than on the basis of beta-gamma activity measurements.

The relationship between the LU concentration and the alpha activity of the core samples as shown in Figure 7 is similar to that between the LU content and the beta-gamma activity. Above 6 ppm LU the alpha activity is approximately proportional to the LU content of the samples. Below 6 ppm this proportionality no longer holds, the contribution to the alpha activity of the members of the uranium series being overshadowed by the contribution from the members of the thorium series. A slight gain in ease of outlining uranium anomalies would thus be experienced by measuring the alpha rather than the beta-gamma activity of the samples in the field.

ACKNOWLEDGMENTS

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COMMENTS ON THE GEOCHEMICAL IMPLICATIONS OF LEAD–ISOTOPE DATING OF GALENA DEPOSITS

DENIS M. SHAW

Several stimulating papers (1, 2, 3, 4, 5) on lead isotopic ratios in galena have recently confirmed that although the ratios of radiogenic isotopes to lead 204 vary considerably, they vary in a regular manner. Apart from certain anomalous figures, isotopic ratios of ores from a given district and geological epoch are constant and are believed to measure the age of the mineralization. Moreover the data from galena of widely different ages are consistent with the hypothesis that most lead deposits come from a common source whose uranium/lead and thorium/lead ratios have changed during geological time only as a result of radioactive decay. The assumption that this source was established during the origin of the earth has enabled several estimates of the age of the earth to be made (5, 6, 7).

It has further been suggested that the source of most lead deposits lies in the mantle rather than in the crust, since the latter is insufficiently homogeneous. For example (4, p. 4)

"—lead ores have risen from a uniform source. Since the composition of the crust is far from uniform, this source is presumably below the earth's crust."

and (3, p. 439)

"our present knowledge of the behaviour of lead isotope abundances and the nature of the earth makes the derivation of lead ores from the upper part of the mantle plausible, and their derivation from crustal rocks highly improbable."

The writer believes these conclusions to be based on insufficient evidence.

TABLE 1

	Pb 204	Pb 206	Pb 207	Pb 208	Age $\times 10^{-9}$ year
Primeval lead, Canyon Diablo	1	9.46	10.34	29.44	4.55
Present-day lead (Wilson et al., 4)	1	18.8	15.8	39.1	0
Ocean sediment lead (Patterson, 10; also compare Patterson et al., 11)	1	19.0	15.8	—	0

Patterson (10) has presented evidence that meteorites are of the same age as the earth and that the lead isotope ratios (Table 1) of the Canyon Diablo meteorite may be taken for primeval earth-lead. Table 1 also includes the ratios for present-day lead and shows that the crustal abundance of lead has increased by about 50% during geological time (if it is assumed that the "age" of meteorites can be roughly equated to the extent of geological time).

The lithophile properties of uranium and thorium probably led to their concentration in the outer zones of the earth during the primary differentiation: lead would partly be concentrated near the surface but most would remain in the inner metal and sulfide phases (13, p. 138). This first differentiation established the early crust containing lead, uranium and thorium in certain quantities. The ratios of these quantities, and assumptions of their constancy or near-constancy for the whole crust or mantle (12, 8, 6, 7), form the basis of lead-age interpretations. Below the continental diorite-tonalite crust lay a basaltic zone containing much less lead, uranium, thorium. Whether or not the original outer crust was initially smaller than at present, growing since by accretion, does not affect the argument.

The early continental crust probably contained galena deposits and radioactive deposits, but their quantitative significance, as now, was negligible. By far the greater part of the lead, uranium and thorium was carried in the original over-saturated igneous rocks. Lead occurred mostly in accessory sulfides, iron oxides, micas and feldspars. Uranium and thorium were in accessories such as zircon, sphene, apatite, and in intergranular compounds. The lead was probably close to the Canyon Diablo figures in isotopic composition, but, as time passed, radiogenic lead accumulated at radioactive atomic sites. During erosion, transportation, and deposition, a thorough mixing of both kinds of lead took place. The ensuing sediments contained lead with isotopic abundances characteristic of the time of deposition, although the lead-uranium and lead-thorium ratios established for the parent rocks were now disturbed as a result of partial separation of the three elements in gradational processes.

According to circumstances, the sediments then either persisted over long periods of time or were subjected to metamorphism and orogenesis and renewed erosion, these processes repeating at intervals until the present day. Each time a mountain range was peneplained the consequent sediments received the lead from pre-existing sediments plus an increment of radiogenic lead from the decay of the uranium and thorium occurring in the sedimentary and igneous rocks eroded. Two situations are possible.

The first is that the overall lead/uranium and lead/thorium ratios for a given mountain-belt represent the original crustal ratios, modified only by radioactive decay. This implies no permanent separation of the three elements (during gradation, vulcanism, and diastrophism) over a broad segment of the crust. The second is that a separation did indeed take place.

In the first case an isotopic analysis of a suitable sedimentary lead would serve to date the time of deposition. To be suitable, the uranium and thorium content must be so low that no appreciable addition of radiogenic lead has occurred (by decay) since deposition. A limestone might meet this requirement. Moreover in the first case each cycle of erosion would contribute an increment of lead to the ocean, whose isotopic ratios would thus measure the age of the crust at any time. In the second case this is not possible. The only sediment that has been measured is the present-day ocean sample listed in Table 1. Its isotopic ratios are consistent with the assumptions necessary for lead-age methods (10) and it may tentatively be concluded that the first alternative is probably correct.

Parenthetically it may be observed that there is here a valuable basis for dating sediments, if technical difficulties can be overcome.

Accordingly it will be taken that, apart from expected local anomalies (similar to the anomalous galenas), there is a possibility that the isotopic proportions of lead in certain sedimentary rocks are principally a function of their age.

Four principal hypotheses of sulphide ore genesis are familiar to geologists. They are not necessarily mutually exclusive and no single one is likely to account for all deposits. They are (a) lateral secretion or metamorphic differentiation, (b) refusion of parts of the crust giving rise (eventually) to magmatic ore-fluids, (c) ore-fluids derived from a magmatic intrusion coming from an unspecified source, (d) ore-fluids or vapors rising from below the crust but unaccompanied by magmatic activity. The first two necessitate a recycling of crustal material; the others do not.

It is probable that lateral secretion from sediments is a valid process for the formation of some sulfide deposits, including galena. Whatever the mechanism of such ore-formation it is improbable that the isotopic proportions of a heavy element such as lead would be materially changed during transfer.

Moreover it is again probable that magma genesis from sediments takes place in the depths of a tectogene, and that hydrothermal ore-forming fluids are evolved during the subsequent magmatic evolution. Such fluids can give rise to some types of galena deposits. There is abundant geochemical evidence now that sediments contain entirely adequate amounts of many metals for either supposition (e.g., 14).

In either case the galena deposited would have isotopic ratios characteristic of the parent sediments. Either process might be expected to lead to thorough mixing before deposition so that local anomalies in the sediments would be minimized. Moreover the sulfide-forming fluids would be unlikely to carry much uranium or thorium, neither being chalcophile. The lead isotope abundances in the galena deposited would therefore give a reliable measurement of the age of the parent rock, modified only by the small amount of radiogenic lead which accumulated by direct decay since the time of deposition of the sediment.

The present crustal abundance of lead is 15 ppm (13). Since the beginning of geological time the abundance has increased by about 50 percent (see Table 1), that is by 5 ppm. Using the figures quoted by Wilson, Russell and Farquhar (5, p. 313) the writer estimates the present crustal abundances of uranium and thorium to be 2.4 and 10 ppm, respectively. Neglecting U-235 and assuming Patterson's (10) earth-age of 4.55×10^9 years, the original abundances of uranium and thorium were 4.8 and 12.5 ppm. The decrease in abundances during geological time are therefore 2.4 and 2.5 ppm. Neglecting the difference in atomic weights of the three elements these figures are the increase in abundance of Pb-206 and Pb-208, totalling 4.9 ppm and showing suspiciously close agreement with the increase obtained from the lead abundance alone. Perhaps the individual figures are uncertain, but the order of magnitude is correct. This result appears to confirm both the confidence to be attached to the abundance figures and the hypothesis of crustal origin of

lead ores outlined above. It should be mentioned that the abundance figures all relate to igneous rocks, as is customary, but since many of the igneous rocks undoubtedly formed by regenerative processes the argument is not nullified.

The possibility remains that some lead deposits were derived from a source independent of and below the present crust, either accompanying igneous activity or by some other process. Without specifying the process it cannot be stated whether lead alone would be added to the crust or whether uranium and thorium would also be introduced. Likewise it cannot be stated whether the quantities added would be sufficient to influence the crustal element balance. In any event the preceding discussion shows that it is not necessary to postulate a sub-crustal source for galena deposits. The crust is admittedly heterogeneous, but crustal processes, especially gradation, diastrophism and vulcanism, tend to restore homogeneity. Anomalous galenas remain a problem to be solved by further information.

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RAMSDELLITE: NEWLY OBSERVED IN MINNESOTA[1]

CYRUS KLINGSBERG AND RUSTUM ROY

ABSTRACT

Chisolm, Minnesota, is recorded as a second locality for the mineral ramsdellite. A possible origin for the mineral assemblages found is suggested.

RAMSDELLITE, an orthorhombic modification of MnO_2, has been identified as occurring in a manganiferous band in the Biwabik formation. A sample was collected by Dr. R. I. Harker at the Monroe-Tener Mine near Chisolm, Minnesota, during a field trip planned at the time of the Annual Geological Society of America meeting in Minneapolis in 1956. The type locality for ramsdellite is Lake Valley, New Mexico, and prior to the present observation no second specific locality for this mineral has been established.* Ramsdellite was first described by Ramsdell (1932), the powder x-ray pattern has been given by Fleischer and Richmond (1943) and the crystal structure determined by Byström (1949).

The small hand specimen received in this laboratory consists of clusters of radiating shiny black crystals (about 6 mm long), embedded in a dull gray matrix. Each portion gives a black streak. However, when ground, the shiny crystals, which prove to be ramsdellite, retain their color whereas the matrix appears dark red-brown. The ramsdellite crystal aggregates characteristically fall apart under finger-tip pressure and the matrix although a little harder breaks up almost as easily.

X-ray fluorescence analysis indicated that the heavy metal content of the matrix is about 20% Mn and 80% Fe with no other elements > 1 percent. It was found that the heavy metal content of the ramsdellite crystals is almost pure manganese with only a trace of iron ($<<1\%$).

The X-ray powder pattern obtained with a Phillips wide-range diffractometer with both filtered CuKα and FeKα radiation is shown in Table 1. For all intents and purposes this is identical with the pattern of Fleischer and Richmond, except that the present sample is much less contaminated and that the weakest reflections are absent in our pattern. This may be ascribed possibly to both better crystallinity and the fact that our pattern is a diffractometer one whereas the older one is a film pattern. These reasons may also be cited to explain the appearance of a relatively strong 020 peak at 4.64Å which has not been recorded in any of the previous patterns. The a and b unit cell lengths obtained from an internally calibrated slow scanning measurement of

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* The Editor has called our attention to a paper which appeared while this work was being done in which the second locality for ramsdellite was reported by P. L. Allsman (Mining Eng., v. 8, p. 1110–1112, Nov., 1956).

a few peaks were calculated since this sample appears to be exceptionally pure. They are not very different from those given by Byström:

	Byström	Present work
a.	4.53Å	4.518_4Å
b.	9.27Å	9.269_8Å
c.	2.86Å	

The fact that two polymorphs of MnO_2 occur side by side (where the relationships suggest that the manganese is probably all of one generation) needs to be discussed.

Interesting geochemical relationships are illustrated by the occurrence of the various phases in intimate contact. The matrix was found to consist of

TABLE 1

X-RAY DIFFRACTION DATA

Ramsdellite (ref. 1) Lake Valley, N. M.			Ramsdellite (ref. 2) Lake Valley, N. M.		Ramsdellite, Chisholm, Minn.	
d(*kX*)	*hkl*	Obs.	*d*(Å)	Int. est.	*d*(Å)	$\frac{I}{I_0}$
	020				4.640_5	49
					4.44	7
4.10	110	v.st.	4.08	10	4.062_3	100
					3.514	7
3.232	120	w	3.20	1		
			3.10*	9		
2.535	130	v.st.	2.53	8	2.547	60
2.436	021	st.	2.40*	4		
2.343	111	m				
2.329	040	m	2.32	4	2.3174	62
2.143	121	st.				
			2.13*	5		
2.058	140	st.	2.09	3	2.063	13
			2.04	2		
			1.95	1	1.964	4
1.903	131	st.	1.88	5	1.870	7
1.796	041	w	1.82	2	1.818	5
1.713	150	m				
1.670	141	v.w.			1.672	5
1.656	221	st.	1.64	6	1.658	3
1.616	240	v.st.	1.60	7	1.619	11
1.542	060	v.w.	1.53	3	1.544	5
1.537	231	w	1.52	2		
1.479	151	v.st.	1.46	5	1.472	5
1.429	002	m	1.42	3		
	330					
1.357		v.st.	1.35	5		
	061					
1.320	311	w+	1.31	2		
1.270	170	m			1.271	7
1.246	132	m				
1.216	042	w−				
					1.182	5
					1.161	11

* Due to pyrolusite (β-MnO_2).

goethite finely admixed not with ramsdellite but pyrolusite (β-MnO_2). From a rough estimate of intensities of the peaks for these two phases and considering the 80:20 Fe:Mn ratio in the matrix it was obvious that not much Mn could be present in the FeO.OH. Slow-scanned powder patterns of the FeO.OH were run and compared with a literature value for synthetic goethite. No significant shift in "*d*" values was observed. The most intense MnO_2 spacing was also unaltered as determined by comparison of $2°\ 2\theta$/min patterns. Other reflections were too weak to be measured accurately.

FIG. 1.

It is not unreasonable to expect considerable solid solution of Mn^{3+} in the goethite structure (with which ramsdellite and probably groutite is isomorphous) and it is conceivable that at the time of formation the manganese invasion of the host rock resulted in such a solid solution. Otherwise, it is difficult to explain the presence of the two polymorphs of MnO_2 together. The postulated relations can be best explained by using Figure 1. The goethite solid solution decomposes to pure goethite and β-MnO_2, while the groutite may be oxidized in situ to ramsdellite, the change involving only the loss of a proton. Experimental work to verify some of these suggestions is in

progress, and the conversion of groutite to ramsdellite has actually been effected in this laboratory.

ACKNOWLEDGMENTS

This research was performed incidental to research on the system Mn—O—OH under the sponsorship of the Signal Corps Engineering Laboratories, Contract DA-36-039, SC-71214.

PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PA.,
Feb. 19, 1957

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PIPE–LIKE ORE BODIES IN PLUTONIC ROCKS

GEORGE VIBERT DOUGLAS

ABSTRACT

The origin of the pipe-like ore deposits in plutonic rocks is considered. An experiment using hot wax and compressed air is described.

In the study of ore deposits, of the type designated as hypogene and epigenetic, curious pipe-like bodies are sometimes encountered.

In some cases these occur at the intersection of two faults or joints. More rarely the pipes occur in massive plutonic rock where there is no fracturing that might have determined the locus of the pipe.

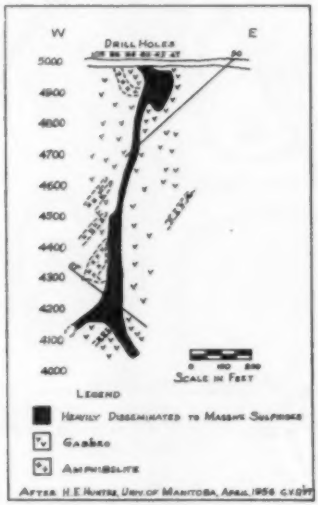

FIG. 1. Sherritt Gordon Mines, Lynn Lake Property. Lateral section of "E" Orebody.

Various examples of these pipe deposits are given by Lindgren (1), Bateman (2), Beyschlag, Vogt and Krusch (3) and Wagner (4). Recently the present writer's attention was drawn to a remarkable example of such a deposit at Lynn Lake in Manitoba. This deposit has been described by H. E. Hunter in an unpublished thesis submitted to the University of Manitoba. Through the courtesy of the Department of Geology of that University, the thesis was made available and the accompanying section (Fig. 1) was copied from it.

The problem that arises is how such a pipe was formed in a massive plutonic rock. The basic idea suggested in this present paper is that such pipes were formed by the rise of gases either as bubbles or as a stream through the magma while it was still fluid.

It is known that hyperfusibles are associated with magmas. A further source of fluids is associated with the boiling out of liquids trapped in the stoping process by which the magma became emplaced.

The following experiment was conducted in the laboratory: A breaker was filled with melted paraffin wax. A tube, with an orifice of about 1 mm diameter was inserted at one side of the beaker so that the orifice was cen-

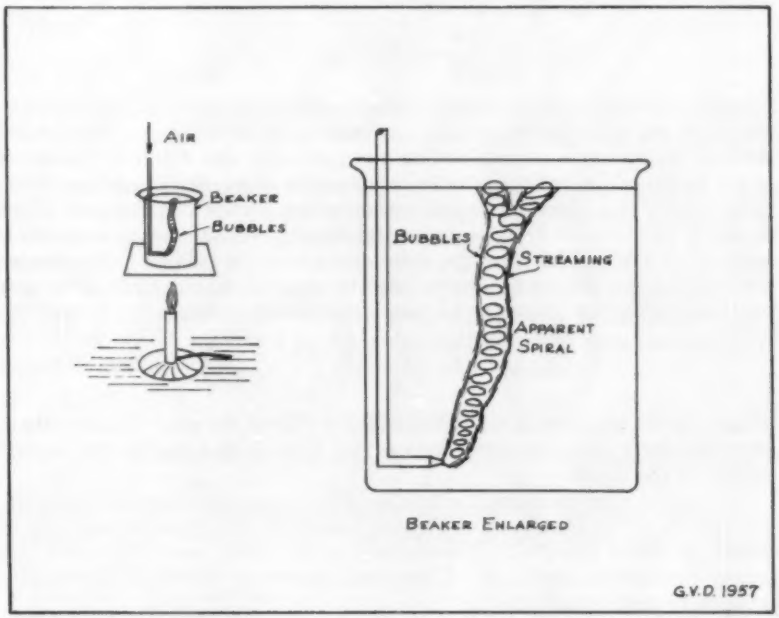

FIG. 2.

trally placed. This tube was connected with a source of compressed air and bubbles of air were forced through the molten wax. The heat source was removed and the wax gradually cooled from the walls inwards. The bubbles rose in a continuous stream and as the viscosity increased with the cooling of the wax, it was seen that there was a continuous tube through which the bubbles passed in their upward passage. As far as could be observed there was also an upward streaming of the molten paraffin along the walls of the tube. The bubbles kept the tube open and continued to pass upwards until the whole beaker became a solid mass (Fig. 2). The tube appeared to have a tendency to spiral. This helical path has been noted by Miyagi as reported

by Lane and Green (6). After the paraffin had completely consolidated the wax cylinder was removed and sawn vertically in two parts. The pipe had continued to exist and showed a certain amount of swelling and pinching. These irregularities can be accounted for by differences in the cooling of the wax or magma. If a zone tended to cool above a hotter one, the gas would expand in the hot zone and then pass through the reduced channelway at a greater velocity. The wax further showed that there was a tendency for it to branch out near the top. Some of the Lynn Lake sections show this branching or fingering in a remarkable way.

The question of the forces involved arises. Lane and Green (6) state that the upward force due to buoyancy is

$$\frac{4}{3}\pi\gamma^3 g(\rho_1 - \rho_a),$$

where γ is the radius of the bubble, ρ_1 the density of the liquid, ρ_a the density of the air or gas in the bubble, g is the acceleration due to gravity. This upward force is opposed by a surface tension given as $2\pi R\gamma \text{ Cos } \theta \cdot f(R/a)$, where R is the radius of the orifice, θ the angle of contact at the liquid-solid-gas interface, $f(R/a)$ is a shape factor and γ the surface tension of the liquid. This opposing force cannot be evaluated unless the shape of the orifice in nature is known. It really determines the shape and size of the bubbles. These same authors give the theoretical terminal velocity of small bubbles. These bubbles act like small falling spheres and Stokes's law should apply.

$$\text{Velocity} = \frac{2\gamma^2 g(\rho_1 - \rho_a)}{\eta}\left(\frac{3\eta + 3\eta'}{2\eta + 3\eta'}\right),$$

where η is the viscosity of the liquid and η' is that of the gas. These authors state that there are some corrections to this formula that involve the surface tension of the liquid.

For a first approximation the density of the magma is taken as 3.0 and the gas as zero. The Handbook of Physical Constants (7) gives the viscosity of diabase as 400 at 1,400° C. The viscosity of air is very small 300×10^{-6} and is neglected in this calculation. Using these figures the velocity of the bubbles is about 15 cms/second.

In the experiment the bubbles had a radius of about $\frac{1}{2}$ cm and it may be argued that there is a tremendous difference between a stream of bubbles of this size and the dimensions of these pipes in the igneous rock. There is not much data available on the maximum size of a bubble, but those that can be observed in volcanic craters rising to the surface of a mass of liquid magma are certainly many centimeters in diameter.

In the case of a gabbro stock, as cooling takes place the viscosity will increase and a point will be reached when the bubbles will cease to rise in the magma.

It can be seen from Stokes's equation that if η exceeds the value of the numerator the velocity will be less than 1 cm/sec and can be made to approach zero as η increases. It is also apparent that as the radius of the bubble in-

creases so will the velocity. The following Table gives the values of the terminal velocities for bubbles of 1 cm. radius with increasing viscosity:

Viscosity in poises	Velocity in cms/sec
400	14.8
600	9.8
800	7.38
1,000	5.87
10,000	0.58
100,000	0.06

If on the other hand a terminal velocity of 1 cm/sec be assumed and the radius be progressively increased the viscosities will increase accordingly:—

Radius in cms	Viscosity in poises
1	58.8×10^2
10	58.8×10^4
100	58.8×10^6

If a terminal velocity of 1 mm/sec be taken, the viscosity could be as high as 58.8×10^7 poises, which value is comparable with that for obsidian at 1200° C (*7*).

The presence of vugs or cavities in lavas or plutonic rocks indicates the point in the cooling of the magma when the value of the viscosity became so large that the upward passage of the bubble was arrested.

Furthermore all that is necessary to ensure a possible pipe of large cross section is the existence of one pipe of sufficient size to allow the passage of a hydrothermal solution. Once this through-going solution is established, its lateral extent can be accounted for by metasomatism or the rising velocity of the ore bearing fluid.

ACKNOWLEDGMENTS

The writer is indebted to Professor W. J. Chute for laboratory facilities and to Prof. A. F. Chisholm for draughting a figure. Mr. G. C. Milligan of the Department of Mines and Natural Resources, Manitoba, discussed the problem with the writer but is not in any way involved in the solution suggested.

DALHOUSIE UNIVERSITY,
HALIFAX, NOVA SCOTIA,
March 28, 1956

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SCIENTIFIC COMMUNICATIONS

PHOSPHATE CONTENT OF SEDIMENTS NEAR BIRD ROOKERIES IN SOUTH FLORIDA

ERNEST H. LUND

The numerous guano-producing islands of the Pacific Ocean, such as the Guanape Islands of Peru with an initial reserve estimated at over a million tons of phosphatic guano, adequately demonstrate the ability of large colonies of birds in concentrating phosphorus. The effect a large population of wading and swimming birds has on the phosphorus content of the sediments near the population centers is less well known.

Samples of sediments from the vicinity of four bird rookeries along the coast of southwest Florida were analyzed for P_2O_5 to determine the effect of the birds on the phosphorus content in the sediment. For comparison samples were taken from other areas in which there were no large bird concentrations. The four rookeries that were used are on mangrove islands and are well suited for this sort of study, because there is a periodic removal of the droppings by high tides, and as many as 80,000 ibis, herons, cormorants, and pelicans may be concentrated on an island of five or six acres.

The amount of phosphorus in the sediments at three of the rookery localities, Green Key, Duck Rock, and East River, is not sufficiently high to conclude that the birds had an appreciable effect on its accumulation. Six samples from Green Key on the east side of Tampa Bay are composed predominantly of quartz sand with varying amounts of silt and clay size material. The P_2O_5 contents, based on dry sample, range from 0.18 percent to 0.46 percent. Eight samples of a mixture of calcareous mud and sand from Duck Rock at the southern end of the Ten Thousand Islands have P_2O_5 contents ranging from a trace to 0.29 percent. Similar material from an unnamed island with no bird colony about a mile north of Duck Rock has from a trace to 0.41 percent. At the East River rookery in the Everglades National Park the sediment consists of a mixture of shell-bearing lime mud and peat. The lime mud is referred to locally and in this paper as marl. Four samples have from a trace to 0.24 percent P_2O_5.

The highest concentrations were found in the vicinity of the Cuthbert Lake rookery located near the southern tip of the state in the Everglades National Park. The mangrove of this small rookery island in Lake Cuthbert grows on a substratum of peat 3 feet thick, and below the peat there is a 14-inch layer of marl. The bedrock is Miami limestone.

Over most of its area the Cuthbert Lake bottom is on Miami limestone. The limestone has a solution-pitted surface, and in many of the depressions

there is an accumulation of shells, limestone fragments, and other debris. The limestone is covered by marl only around the margins of the rookery island and around the fringes of the lake. The marl is thinner away from the edge of the mangrove and generally extends less than 100 feet out into the lake. This condition suggests that erosion instead of sedimentation is more effective in the main body of the lake.

Although there is essentially no deposition in the vicinity of the rookery island, there is precipitation of phosphate. In addition to peat, marl, and shell, samples from this locality contain small concretion-like particles of phosphate material. A sample submitted to J. B. Cathcart and analyzed by George Ashby of the U. S. Geological Survey showed apatite the major mineral phase. Fluor-apatite is indicated by its fluorine content. The particles range in size from less than 1 mm to about 2 cm. They accumulate in the limestone solution pits beyond the edge of the marl and on the island's beach which is exposed at low tide. The phosphate particles were not found in peat and marl samples taken from the middle of the island, and none was found in the samples collected from the fringe of the lake, although the sediment there is otherwise similar to that near the rookery island.

Eleven samples collected at a distance of 20 feet to 70 feet from the edge of the rookery island contain varying amounts of peat, marl, shell fragments, bedrock fragments, and phosphatic particles. The P_2O_5 contents of these samples range from 0.48 percent to 7.92 percent with an average of 4.10 percent. The amount of phosphorus varies with the quantity of the phosphatic particles in the sample. A sample from the island's beach, consisting almost entirely of ground up peat and phosphate, has 24.55 percent P_2O_5 based on dry sample. This sample had a 25.50 percent ignition loss, and when the P_2O_5 is based on ash, the value is 33.77 percent.

The amount of phosphorus in the sediment near the rookery contrasts sharply with that in the sediment from around the edge of the lake. Four samples of marl from widely separated points near the lake's edge contain P_2O_5 ranging from a trace to 0.18 percent. The distribution of phosphorus in the sediments of Cuthbert Lake indicates that the bird colony plays an important role in its accumulation.

FLORIDA STATE UNIVERSITY,
TALLAHASSEE, FLORIDA,
March 9, 1957

DISCUSSIONS

A DEFINITION OF COAL

Sir: As James M. Schopf [1] has criticized my definition of the term "coal," may I, in my turn, criticise the definition proposed by him. First of all I would like to point out that the length of a definition must be judged in relation to the size and scope of the publication in which it appears. In a concise dictionary coal may be defined in one sentence, while in a scientific encyclopaedia a much more extensive treatment is needed. The definition criticised by J. M. Schopf appears in a glossary of terms exclusively devoted to coals and bitumens, from which all references to industrial uses and methods are rigidly excluded. This is why, in my definition, such an obvious property of coal as that of being a "combustible substance" is not mentioned at all, because this is already implied in the adjective "carbonaceous."

J. M. Schopf, unfortunately, does not give my definition in full. In fact he quotes only the first sentence. My definition, which is rather extensive, deals with five aspects of coal: (1) geological, (2) structural, (3) chemical, (4) comparative and (5) classificatory.

The full text, divided up into the five sections, is as follows:

"(1) A stratified carbonaceous rock formed through the accumulation of vegetable debris, together with the product of their decay of varying degree of completeness, and the whole subjected to a certain amount of metamorphism conditioned by moderate pressure and moderate heat.

(2) From the structural point of view coal is a compressed mass of fragment of plant tissues and other plant substances, such as resins, the whole being immersed in an amorphous mass of degraded products.

(3) From a chemical point of view coal (including peat) is composed mainly of carbon, varying from 50% to 98%, hydrogen, varying from 3% to 13%, oxygen and a certain amount of sulphur, nitrogen and ash.

(4) In contrast to bitumen, coal is always found in the place of deposition of the original plant material.

(5) The nature of the original plant material determines the type of coal, while the degree of metamorphism determines the rank."

S. I. Tomkeieff. Coal, and bitumens and related fossil canfonaceous substances. Nomenclature and classification. Pergamon Press Ltd., London, 1954, p. 38.

[1] James M. Schopf, 1956, A definition of coal: Econ. Geol., 1956, v. 51, no. 6, p. 521–527.

Here is the definition of coal proposed by Schopf:

"Coal is a readily combustible rock containing more than 50 percent by weight and more than 70 percent by volume of carbonaceous material, formed from compaction or induration of variously altered plant remains similar to those of peaty deposits. Differences in the kinds of plant materials (type), in degree of metamorphism (rank), and range of impurity (grade), are characteristic of the varieties of coal."

My criticism of this definition, point by point, is as follows:

1. Not all coals are "readily combustible." Anthracite, for example, is not.
2. Limitations of coals by percentage weight or percentage volume of carbonaceous material is, in my opinion, purely arbitrary and has no justification in actual practice.
3. "Compaction or induration" should be "compaction and induration."
4. "Plant remains similar to those of peaty deposits." This applies only to bituminous coals. Sapropelic coals are not made of peaty materials.
5. The term "grade of coal" is not restricted to the content of impurities such as ash and sulphur, but may apply to any other technological aspect of coal, such as the volatile content or thermal efficiency.

In criticizing J. M. Schopf's attempt to produce a revised definition of coal, I welcome his *desideratum*, that:

"A definition should be applicable to all subjects included and nothing else; it should state essential attributes; it should refer to the category to which the subject belongs and it should differentiate the subject defined from others within the same category."

In my modest opinion, my own definition of coal has fulfilled all the conditions of this *desideratum*. The technological aspect, as explained above, was not included because it fell outside the scope of the glossary in question. It is, however, very important and, if mentioned at all, should say not only that coal is combustible, but also that it can be burned to provide heat, carbonised to provide coke, distilled to provide coal-tar and all its by-products, and so on.

S. I. TOMKEIEFF

KING'S COLLEGE,
UNIVERSITY OF DURHAM,
NEWCASTLE UPON TYNE, ENGLAND,
March 12, 1957

A DEFINITION OF COAL

Sir: Dr. Tomkeieff's definition of coal has many good points and, as far as it goes, may be useful. The reasons for preferring the definition I gave are stated in my paper cited previously. An arbitrary standard is required to differentiate coal from less carbonaceous rocks. A definition is less useful if it fails in differentiation.

Among the points with which Dr. Tomkeieff takes issue, his statement that sapropelic coals are not made of peaty materials is most surprising. Sapropel

is one of the important types of bio-clastic ("peaty") deposits. Microscopic evidence shows all coal had its origin from peaty materials. Thus, a great variety of plant substances is included, some of which are imperfectly segregated in certain deposits. In spite of segregative differences, however, all these deposits contain a variety of plant remains which indicate they had their origin from one or another of the many different types of peat.

In formation of coal, compaction and induration are related, but induration lags behind compaction. Both terms are difficult to quantify, but the phrase "compaction or induration" seems more appropriate in view of the compacted but scarcely indurated condition in coals of low rank.

I have indicated that coal is a readily combustible rock, but Tomkeieff says not all coals are readily combustible. Anthracite, he says, is not. Although anthracite often is difficult to *ignite*, many users of anthracite attest to the fact that anthracite readily supports combustion. Since the combustible properties of coal are so important, it seems desirable to mention this characteristic in a definition for general application.

JAMES M. SCHOPF

U. S. GEOLOGICAL SURVEY
COLUMBUS, OHIO
April 29, 1957

URANIUM ORE GUIDES, MONUMENT VALLEY, ARIZONA

Sir: I wish to make some comments regarding the article entitled, "Structural control of uranium ore at the Monument No. 2 mine, Apache County, Arizona," (ECON. GEOL., vol. 52, No. 4). Tommy L. Finnell, the author, should be informed that a similar article appeared earlier in this bulletin (4).

TWO VALID VARIATIONS

The earlier article was mainly a compilation but contained a number of original observations and concepts. Stated in general terms, one of the hypotheses presented (p. 174–175) was as follows:

Fractures and fracture patterns on Shinarump-capped mesas may be an indication of buried channels at the base of the Shinarump. One should expect fractures in the vicinity of channels to be different from surrounding fractures. During regional folding, locally imposed stresses due to the anomalous sedimentary structure (the relatively competent channel filling) would account for this difference.

The emphasis of Mr. Finnell's conclusions was, in general terms, the same as the original concept. However, he made no reference to the earlier article. Argument in developing the concept and detailed definition of the concept were interestingly different in the two articles.

The original article discusses the strain behavior of the Shinarump rock body itself in the vicinity of thickened channel-filled areas. This rock body is considered as a brittle thin-plate, covered and underlain by rock bodies that are relatively plastic in behavior. Bedding-plane slippage is the stress of the

later article, considering interference by the massive channel structure. Actually, both explanations may be valid.

As for fracture differences in channel vicinities, the earlier article suggests the search for anomalous attitudes of fracture planes, while Mr. Finnell suggests the search for zones of en echelon strike-slip faults. Both such anomalies may be valid in Monument Valley.

FIG. 1 Geologic map of the northeast-trending cuesta in the Monument No. 2 area. Cuesta is capped by the basal Shinarump member of the Upper Triassic Chinle formation. Only fractures in the Shinarump are mapped, with the exception of major fractures in pre-Shinarump rocks to the north and west of the channel.

Furthermore, one should note that, forty years ago, Gregory (3) reported uranium deposits in the Monument Valley area as being in the Shinarump, a rock unit recognized by Gilbert (2), with broader stratigraphic definition, in 1886. Baker (1) has described Monument Valley geology in considerable detail.

TRANSVERSE FRACTURES

Finnell's statement that prominent joints in the *area* trend N 35°–65° W appears to be a misleading oversimplification.

When first observing the Comb Ridge monocline, in the general area and to the south and east, one quickly notes an exception to the rather common rule of Colorado Plateau monoclines. Longitudinal fractures are not dominant over transverse fractures. The two systems are about in equal prominence.

Furthermore, on the Shinarump cuesta, within a few miles of Monument No. 2 mine, longitudinal fractures are rare whereas transverse fractures are quite dominant. To a large extent, this phenomenon is a function of the characteristics of the Shinarump rock body.

This writer spent two days last year mapping the Monument No. 2 area in some detail (Fig. 1), resulting in the following observations:

1. Generally, there are two prominent fracture attitudes on the Shinarump cuesta in the area, striking N 42°–62° W and N 71°–87° W. By weighted means, these are N 54° W and N 81° W. Fractures are near vertical in dip.

2. In and over the Monument No. 2 channel, there are two markedly prominent fracture sets, striking N 33° W *and* N 64° W (± 2 degrees). We assume that these are the sets that influenced Finnell to give a *range* of prominent joints in the *area* of N 35°–65° W. Some sets typical of the area are found over the channel.

3. This contrast, between fracture sets at the channel and sets in the Shinarump of the area, is rather striking and may be quite significant in the search for buried channels.

4. Strikes of beds in the area average about N 10° E. Thus during folding, one would expect two possible tension-shear systems:

Transverse system		Longitudinal system	
tension:	N 80° W*	tension:	N 10° E
shear:	N 50° W*	shear:	N 40° E
	N 70° E		N 20° W

Asterisks denote the theoretical sets that most nearly parallel the two prominent sets observed in the Shinarump of the area, i.e., N 81° W and N 54° W. The two prominent sets at the channel are anomalous, i.e., N 33° W and N 64° W.

Some geologists will not agree with the defined theoretical systems. The definition assumes that, during folding and at different intervals, beds are subjected to both transverse and longitudinal tension. Also, the two shear sets of a system are assumed to be at an angle of 60° to each other, bisected by the attitude of the tension set.

Finally, one might further note that Finnell's speculation, that anomalous channel fractures were feeders for mineralizing solutions, is of doubtful validity. These fractures may well have helped prepare the ground locally, but major fracture zones to the north and west (Fig. 1) would more likely be feeders from depth.

THOMAS W. MITCHAM

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FLAGSTAFF, ARIZONA,
March 6, 1957

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MINERAL RESERVES AND MINERAL RESOURCES

Sir: In their report on Mineral Reserves and Mineral Resources (This Journal, Vol. 51, Pp. 686–697) Blondel and Lasky make a most useful contribution towards the resolution of the confusion surrounding concepts and definitions of magnitudes of mineral raw materials. It is of great benefit to have so clear an expression of the difference between "reserves" and "resources," and it is to be hoped that the distinction is generally adopted. It would be unfortunate if this significant clarification were to languish or be passed over by the geological profession through inertia or the absence of a mechanism for formal endorsement. To a certain extent, however, the terminology "miner" and "economist" used in developing the distinction leads to connotations or implications that we do not think the authors intended.

The authors state that ". . . whereas the miner thinks in terms of the economic present or the economic near future, the economist dealing with resource appraisal thinks of the more distant future and therefore takes into consideration deposits well beyond the miner's present interest" (p. 686). Also, "The terms created by the miner to describe the ore reserves of his mine cannot appropriately be transported into the larger and more indefinite field of inquiry of the economist" (p. 686).

This use of the terms "miner" and "economist" not only can be interpreted as implying that the relevant concept of reserves or resources depends on the *person* who is doing the appraising, but also may suggest to some an unduly narrow purview of both the economist and the miner, particularly the former. The relevant concept of reserves or resources depends, of course, on the *purpose* of the appraiser rather than on his profession. Blondel and Lasky certainly do not maintain otherwise, but to choose professions as descriptive terminology for characterizing an appraiser's purpose may invite additional confusion.

The economist in the authors' presentation seems to be the man with the crystal ball—he looks into "the more distant future"; his field is "larger and more indefinite" than the miner. It is probably true that the economist is more likely to be concerned with national, regional or industry-wide questions than the individual mining engineer, and the engineer, in turn, more likely to be concerned with his company's prospective profits than is the average economist. Yet the economist may be hired by the miner, or the latter may be asked to serve on an industry or government committee to look into questions more far-reaching than those of the individual company or enterprise.

As Blondel and Lasky describe the miner's approach, it involves the present and near term, and can be called a "commercial" view. What they call the economist's approach appears essentially to involve longer term, public policy aspects. Perhaps, instead of "miner" and "economist," the contrasting approaches would be better described as the "commercial" and "public policy" approaches. These terms would not preclude the member of either profession from making use of either approach. The economist could try to make money for his mining employer, for example; or, the miner would be free, in a terminological sense, to perform a public service.

But even this suggested terminology is really too narrow. "Public policy" in mineral raw materials not infrequently involves consideration of factors that depend on and influence present and near term developments. The economist who is looking into such questions as the possible level of mineral production or the kind and extent of mineral price controls desirable under wartime mobilization is more interested in reserves than in resources and in more immediate rather than long-term aspects. It is also true that the "commercial," or miner's approach is not exclusively tied up with present or near term considerations. Decisions to keep a mine operating or to expand facilities are based on expected developments five, ten, or more years in the future, and the magnitude of resources of the mineral or minerals concerned is an important consideration in such decisions.

The foregoing criticism is not meant to detract from Blondel and Lasky's work. We believe, however, that their contribution would be of still greater value if the terminology employed to clarify the reserve-resource distinction emphasized the *purpose* rather than the profession of the interested person. As our note suggests, the purpose often reflects what could be called "commercial" or "public policy" aspects as well as, or as part of short- or long-term time dimensions.

Bruce C. Netschert
Donor M. Lion

Washington, D. C.,
April 29, 1957

REVIEWS

Lectures on Rock Magnetism. By P. M. S. BLACKETT. Pp. 131. Interscience Publishers, Inc., New York, London and Jerusalem, 1956. Price, $5.00.

The book is a printing in Jerusalem of the Second Weizmann Memorial Lectures, delivered at Rehovoth, Israel, in December 1954. It consists of three chapters and three appendices. The first chapter contains the author's ideas of the use of rock magnetic data to trace the history of the earth's magnetic field and the movement of continents. In the second chapter he describes some experimental work carried out in his laboratory at the Imperial College in London on the phenomenon of the reverse magnetism of so many rocks. In the third chapter he comments on results revelant to the movement of land masses and the history of the earth's field. He strongly favors polar wandering and continental drift. The three appendices deal with special experimental methods developed in his laboratory and some results achieved. These subjects are "A New Magnetic Measuring Instrument," "The Separation of Small Quantities of Magnetic Materials," and "The Thermal Reversal of Magnetically Treated Materials."

The book is stimulating and thought provoking. It is well known that when rocks are formed they tend to become magnetized in the direction of the magnetic field of the earth. The evidence of magnetic reversals and pronounced changes of the magnetic field in geologic time are supported by much evidence. However, the conclusions to be drawn from this data may not be considered as conclusive as the factual data. It is a question of interpretation of the factual data. Polar wandering and large-scale continental drift could explain the past magnetic deviations, but is that the only explanation? One cannot but recall that the present day magnetic deviation maps in northwestern Canada show lines of magnetic deviation that are S-shaped with deviations of 90 degrees or more from the magnetic north. If sediments were to be deposited today in such areas would they not show anomalous directions of magnetization? If in the past similar magnetic deviations had existed would not those old rocks show quite different magnetization from the general magnetic field of today?

A. M. B.

L'Évolution de la Lithosphere, II Orogénèse. By HENRI TERMIER and GENEVIÈVE TERNIER. In two parts. Pp. 940; figs. 152; maps 86. Masson et Cie, Paris, 1956. Price bound, each volume 9,800 francs.

These two monographic volumes are a part of the authors' Traité de Géologie of which the first (1952) is the Histoire Géologique de la Biosphère. The second (1956) is L'Evolution de la Lithosphère, I, Pétrogénèse, and the third is the one under review. The fourth is in preparation and will be a continuation entitled, III, Glyptogénèse et Sédimentation. Others are to follow.

The present Orogénèse is divided into 1) generalities, dealing with earthquakes, earth movements, deformation and structural analyses; 2) the oceans; 3) the continents "Laurasiens," including North America, Greenland, and Asia; 4) the conti-

nents "Gondwaniens"— Africa, India, Australasia, Antarctica, and South America; 5) Tethys; and 6) "Essai de Megatectonique."

The authors cover the history of all known orogenies since early Precambrian. Each orogenic period and area are discussed in detail, followed by conclusions and a bibliography. The last part is a general review of orogeny based upon the preceding discussions, and treats of their classification, evolution, orogenic theories, relationships to each other; and evolution of the lithosphere.

The volumes are well illustrated with many sketches, cross-sections, and folded plates. The work is an outstanding monographic treatment and should stand as the leading book on orogeny.

Earth Flexures. By H. G. Busk. Pp. 106; figs. 92. William Trussell, New York, 1957. Price, $3.50.

The title also states "Their Geometry and Their Representation and Analysis in Geological Section with Special Reference to the Problem of Oil Finding." The book is an unabridged republication of the 1929 edition by the Cambridge University Press. Its six chapters deal with geological processes of folding and sedimentation and definitions of them, geometrical construction of flexures, the location of axial planes underground, geological mapping for sections, examples of Tertiary flexures in Burma, Iran and rift valley country. Since this book is just a reprinting of the 1929 edition, it does not of course include the later information disclosed particularly in the Middle East.

Properties of Petroleum Reservoir Fluids. By Emil J. Burcik. Pp. 190; figs. 103. John Wiley and Sons, New York, 1957. Price, $7.50.

Petroleum engineering is constantly changing and enlarging and this book attempts to bring the subject up to date starting from the basic concepts, which are treated in logical sequence as far as reservoir fluids are concerned. The approach is from ideal conditions to a realistic approach to the complex systems of reservoirs. The chief topics treated are properties of petroleum deposits, behavior of gases and phase behavior of liquids, qualitative and quantitative phase behavior of hydrocarbon systems, reservoir fluid characteristics. Three appendices give symbols and abbreviations; physical and thermodynamic properties of methane, ethane, propane, butane, and pentane; table for conversion of A.P.I. to specific gravity. There are incorporated all data, tables, and correlation charts to solve the common problems of petroleum engineering. It should prove a useful book to petroleum engineers.

Précis de Géomorphologie. By M. Derruau. Pp. 394; figs. 164; plates 50. Masson et Cie, Paris, 1956. Price bound, 3600 francs.

The author has written this book for an advanced text book and reference work on geomorphology. In an introduction, he presents some general features of the subject and methods of study. The remainder of the book is divided into 5 sections. The first (22 pp.) deals with the constitution and movements of the earth's crust, involving seismology, gravity, orogeny, sedimentary basins and theories "mobilistes" and "fixistes." The second section, entitled "L'Érosion Dite Normale" (72 pp.), considers the customary features of erosion by rain wash and streams, and cycles of erosion. The third section is "Les Systèms D'Érosion Morphoclimatiques" (88 pp.) wherein the author treats of paleoclimates, glaciation, desert, interior, and tropical and subtropical erosion. The fourth and longest section (125

pp.) considers the influence of rocks and their structure in the development of land forms. This deals separately with the influence of detrital, calcareous, crystalline and volcanic rocks. It also includes the effects of different kinds of structures and of sedimentary basins, massifs, and of mountain chains. The last section (36 pp.) deals with the littoral and submarine features.

The author weaves in nicely the background and development of the earlier ideas of geomorphology, the classics, and modern thought. It is a well rounded and well organized book. It is a fine piece of printing and is nicely and adequately illustrated with good sketches and photographs.

Landslides in Clays. By ALEXANDRE COLLIN. Translated by W. R. Schriever. Pp. 160; pl. 21. Univ. of Toronto Press, 1956. Price, $6.50.

This classical book was published in Paris in 1846 and became forgotten. R. F. Legget happened to track it down and inspired and assisted in its translation. Mr. Schriever, his colleague, was assisted also by J. P. Carrière and D. H. MacDonald. Dr. A. W. Skempton of Imperial College, London, wrote an introduction analyzing the significance of Collins' work. Collins' theories of landslides apparently are quite close to those of today and he refers to practices in soil engineering which Mr. Legget and Dr. Skempton consider are commonly regarded as modern developments. Mr. Legget also contributes an interesting Foreword. The 12 chapters deal with surveys and field data on shear surfaces, which indicate deep rotational movements. He points out the differences between deep slides and surficial slides and notes cycloidal slip surfaces, which is a type of failure fundamental in clay slopes due to inadequate shear strength.

It is interesting to have republished a translation of a classical work that contains many of the fundamentals of modern knowledge.

Route-Mapping and Position-Locating in Unexplored Regions. By W. FILCHNER, E. PRZYBYLLOK AND T. HAGEN. Pp. 288; figs. 171. Academic Press, Inc., New York, 1957. Price, $9.00.

The three authors of this book come from Munich, Cologne, and Zurich respectively, and the book was printed in Switzerland. It is in English. The senior author had wide experience in Tibet, Nepal, India and Antarctica. This book was initiated in India where he was interned during World War II.

The book is divided into three parts, each by one of the authors. The first part is on route mapping by the senior author, the second is on position finding and altitude measurements by the second author. The third is on route-mapping and topographical surveys with the aid of photographs by the third author. The first part deals with the old-time ground route-mapping equipment, outfits, measurements, and topography in different kinds of terranes. The second is largely astronomic and deals with methods of determining altitudes and azimuths. The third part brings in aerial and ground photography and photogrammetry.

The subject matter is chiefly standard practices, with most examples drawn from little explored areas. The first part is quite elementary, but the reader is charmed by the dialogue type of presentation and the explorers' viewpoint. The reader is told in detail the exact manner in which each step is taken. It is rather long drawn out. The second part is a more condensed presentation of applied astronomy.

BOOKS RECEIVED

JAMES M. ALLEN

Sunken Islands of the Mid-Pacific Mountains. EDWIN L. HAMILTON. Pp. 97; pls. 13; figs. 12; tbls. 5. The Geological Society of America Memoir 64, New York, 1956. *The findings support Darwin's Subsidence Theory for the formation of atolls and furnish evidence for a deep Cretaceous Pacific Ocean and refute the hypothesis of transoceanic "sunken continents."*

Treatise on Marine Ecology and Paleoecology. Vol. 2, Paleoecology. HARRY S. LADD, Editor. Pp. 1077. The Geological Society of America Memoir 67, New York, 1957. *A symposium including the paleontological record and the origin of life, selected analyses from the geologic record, and an annotated bibliography of marine paleoecology.*

Beekmantown Group (Lower Ordovician) of Maryland. WILLIAM J. SANDO. Pp. 161; pls. 15; figs. 20; tbls. 3. The Geological Society of America Memoir 68, New York, 1957. *Faunal, tectonic setting, genetic relations.*

Genus Pentremites and Its Species. J. J. GALLOWAY and HAROLD V. KASKA. Pp. 104; pls. 13, figs. 5; tbls. 5. The Geological Society of America Memoir 69, New York, 1957. *Sixty-three species recognized, ranging in age from Lower Mississippian to Late Mississippian. Three new species proposed.*

British Territories in Borneo. Annual Report of the Geological Survey Department for 1956. F. W. ROE. Pp. 212; figs. 41. Government Printing Office, Kuching, Sarawak, Borneo, 1957. Price, Malay $3.00, or Sterling 7s. *Elaborate and comprehensive report of the geology of Sarawak, Brunei, and North Borneo, and mineral resources of oil, gold, phosphate, bauxite, coal, iron, copper and building materials; abundantly illustrated.*

Geology of the Cuyuna District, Minnesota, A Progress Report. FRANK F. GROUT and J. F. WOLFF, SR. Pp. 144; figs. 24; maps 6. University of Minnesota Press, Minneapolis, 1955. *General summing up of geology; Cuyuna iron ores, their mineralogy, classes, origin, reserves, economics; stratigraphic successions; geologic maps; correlations; emergency manganese; and appendices.*

Geology and Ground-Water Resources of Central-East Georgia. H. E. LEGRAND and A. S. FURCRON. Pp. 174; pls. 2; figs. 14; tbls. 22. Georgia Geological Survey Bull. 64. Atlanta, 1956.

Map of Great Britain Limestone Occurrences, 2 sheets, scale 10 miles to 1 inch. *Distribution of economic limestones; geologic horizons, quality, quarries shown by color and symbols.*

Petroleum Industry in Illinois in 1955: Part I. Oil and Gas Developments. A. H. BELL and VIRGINIA KLINE. **Part II. Waterflood Operations.** P. A. WITHERSPOON and D. A. PIERRE. Pp. 195; figs. 30; tbls. 16. Illinois State Geological Survey Bulletin 81. Urbana, 1957.

Cartography (Map Making). H. A. BAUER. Monograph 60. Pp. 32; pls. 2. Bellman Publishing Co., Cambridge, Massachusetts. *Nature, history, facilities, training.*

Variations in Isotopic Abundances of Strontium, Calcium, and Argon and Related Topics. Pp. 117. Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, 1957. *Results and refinements of geochromometric methods; ages of biotites, glauconite, muscovite, hornblende, radiochemical studies.*

Estudos, Notas e Trabalhos do Serviço de Fomento Mineiro. Serviços Geologicos da Portuguesa. Vol. XI, Fascs. 3–4. Pp. 315; maps and colored plates. *Tungsten minerals, manganese and iron deposits, geochemistry of sphalerite and galena, and administrative reports.*

Outline of Progress of the Mining Industry of the Province of Quebec During the Year 1956. EDGAR-E. BÉRUBÉ. Pp. 17; pls. 5; tbls. 2. Quebec Department of Mines, 1957. *Statistics and new developments.*

The Geology of the Odzi Gold Belt. W. H. SWIFT. Pp. 44; pls. 6; figs. 3. Southern Rhodesia Geological Survey Bull. 45. Salisbury, 1956. *Areal geology of the Southern Rhodesian gold belt. 75 gold mines, 2 copper mines, 5 scheelite mines and 2 arsenic mines of the area.*

The Geology of the Barberton Area. Compiled by D. J. L. VISSER. Pp. 253; pls. 45; figs. 14; maps and sections. Price, £1 15s. Union of South Africa Geological Survey Special Pub. 15. Praetoria, 1956. *Petrology, structure and stratigraphy of the Precambrian rocks of the eastern Transvaal.*

Geologia de las Cuencas Sedimentarias de Venezuela y de sus Campos Petroliferos. G. A. YOUNG, A. BELLIZZIA, H. H. RENZ, ET AL. Pp. 140; figs. 75; tbls. 10. Ministerio de Minas e Hidrocarburos, Republica de Venezuela, Caracas, 1956. *Geology and petroleum potentialities of many districts.*

Bull. 37. Inventory of Washington Minerals. Part II. Metallic Minerals. MARSHALL T. HUNTTING. Pp. 428; 2 vols.; pls. 27. Price, $4.50. Department of Conservation and Development, Olympia, Washington, 1956. *Listing of the various metals, giving properties, uses, production, prices, minerals, geology, and occurrences by counties; Vol. 2 consists of maps showing locations.*

U. S. Department of the Interior, Bureau of Mines Circular 7771. Bibliography of Zirconium. ELEANOR ABSHIRE. Pp. 281. Washington, D. C., 1957. *A complete bibliography and excellent annotations.*

Annual Report of the Director of the Geophysical Laboratory 1955–1956. P. H. ABELSON, Director. Pp. 229. Carnegie Institution of Washington, 1957. *Reports of progress on various projects; digests of results.*

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1956–57.

Explanatory Text of the Geological Map of Japan. Yawatahama and Iyo-Takayama (Kōchi-68.76). KEN HIRAYAMA and NOBUKAZE KAMBE. Pp. 58; figs. 21; maps 2. *Areal geology of Western Shikoku Island. Several small pyritic copper deposits.*

Explanatory Text of the Geological Map of Japan. Kokubu (Kagoshima-82). KONOSUKE SAWAMURA. Pp. 21; maps 2. *Mesozoic sediments of southern Kyushu.*

Explanatory Text of the Geological Map of Japan. Nokogirizaki (Kanazawa-77). OSAMU HIROKAWA and KAZUO KURODA. Pp. 26; map. *Paleozoic, Mesozoic and Cenozoic formations of central Japan.*

Explanatory Text of the Geological Map of Japan. Ohata (Aomori-3). FUJIO UEMURA and MASATSUGU SAITO. Pp. 39; map. *Late Cenozoic formations of the northern tip of Honshu Island.*

Geological Survey of Kansas—Lawrence, 1956–57.

Bull. 119, Part 7. Relation of an Airborne Magnetic Profile to the Geology Along the Kansas-Nebraska Border. D. F. MERRIAM and W. W. HAMBLETON. Pp. 14; pls. 1; figs. 2; table 1. *Reveals structure including Hugoton embayment, and thickness of post-Precambrian rocks, also Precambrian basement.*

Bull. 119, Part 8. The Mineral Industry in Kansas in 1955. W. H. SCHOEWE. Pp. 49; figs. 3; tbls. 43.

Bull. 121. Stratigraphy and Structural Development of the Salina Basin Area. WALLACE LEE. Pp. 167; pls. 12; figs. 23; tbls. 19. *Precambrian to Quaternary; from outcrops and well logs.*

Bull. 125. Ground-Water Levels in Observation Wells in Kansas, 1956. V. C. FISHEL and B. J. MASON. Pp. 158; figs. 22; tbls. 5.

Kansas Rocks and Minerals. L. L. TOLSTED and ADA SWINEFORD. Pp. 64; pls. 29.

Ohio Geological Survey—Columbus, 1957.

Rept. of Investigations 31. Coal Resources of the Lower Part of the Allegheny Formation in Ohio. R. M. DELONG. Pp. 43; figs. 11; tbls. 24.

Rept. of Investigations 32. 1956 Oil and Gas Developments in Ohio. G. G. SHEARROW. Pp. 29; pls. 2; tbls. 14.

Ontario Department of Mines—Toronto, 1956–57.

Sixty-fourth Annual Rept. Vol. LXIV, Pt. 7, 1955. Pleistocene Geology and Ground-Water Resources of the Township of North York, York County. A. K. WATT. Pp. 64; pls. 13; figs. 5; tbls. 5; maps 3.

Sixty-Fifth Annual Report. Vol. LXV, Pt. 1, 1956. Statistical Review of the Mineral Industry of 1955; Mining Accidents in 1955; Classes for Prospectors. M. G. ARNOLDI, W. D. HARDING, and others. Pp. 78.

U. S. Geological Survey—Washington, D. C., 1956–57.

Bull. 1042-E. Physical Stratigraphy of the Phosphoria Formation in Northwestern Wyoming. R. P. SHELDON. Pp. 80; pls. 5; figs. 18; tbls. 2. *Detailed stratigraphy; environments of deposition; phosphorite deposited at — pH 7.8 and Eh less than — 0.25.*

Bull. 1042-G. Gem Stones of the United States. D. M. SCHLEGEL. Pp. 50. Price, 25 cts. *Properties, cutting, syntheses.*

Bull. 1045-A. Core Logs from Owens China, Searles, and Panamint Basins, California. G. I. SMITH and W. P. PRATT. Pp. 62; pl. 1; figs. 2. Price, 55 cts. *Detailed logs of holes to 995 feet depth; sediments and saline minerals.*

Bull. 1048-D. Geophysical Abstracts 167 October–December 1956. M. C. RABBITT, D. B. VITALIANO, S. T. VESSELOWSKY and others. Pp. 157. Price, 25 cts. *Abstracts of current literature pertaining to the physics of the solid earth and to geophysical exploration.*

Water-Supply Paper 1374. Preliminary Survey of the Saline-Water Resources of the United States. R. A. KRIEGER, J. L. HATCHETT, and J. L. POOLE. Pp. 172; pls. 2; figs. 2; tbls. 7. *A discussion of salinity and a compilation of measurements and chemical analyses of saline ground and surface waters, with an emphasis on their geographic and geologic distribution.*

Water-Supply Paper 1376. Feasibility of Ground-Water Features of the Alternate Plan for the Mountain Home Project, Idaho. R. L. NACE, S. W. WEST, and R. W. MOWER. Pp. 121; pls. 7; figs. 24; tbls. 26. Price, $1.75. *Evaluation of plan to divert water from Boise River to arid plain, water to be replaced by pumping and importing water from Snake River.*

Water-Supply Paper 1410. Geology and Ground-Water Resources of the Lower Lodgepole Creek Drainage Basin, Nebraska. L. J. BJORKLUND and E. R. JOCHENS. Pp. 76; pls. 4; figs. 5; tbls. 11.

SCIENTIFIC NOTES AND NEWS

C. A. U. CRAVEN has left the United Kingdom Geological Survey to enter private practice as a consulting economic geologist in London, England. His address is c/o Westminster Bank Ltd., 1 Brompton Square, London, S. W. 3.

SHELDON L. GLOVER has retired as supervisor of the Washington State Division of Mines and Geology.

PHILIP C. HEWITT has resigned his teaching position at Cornell University and joined the geology department at Union College in Schenectady.

PARKE A. HODGES, vice president of Behre Dolbear & Co., Inc., New York, has been doing professional work in Liberia and Sweden.

ROBERT D. FERRON, Manager of the South American division of Kennecot Copper Corporation's Exploration Department, has changed his headquarters from Lima, Peru, to Rio de Janeiro, Brazil.

P. RAMDOHR, professor of mineralogy and petrology at the University of Heidelberg, Germany, is on a lecture and study tour of the Union of South Africa, in connection with the nature and source of the gold and uranium ores of the Southern Transvaal and Free State. In one lecture Dr. Ramdohr compares "the uranium ores of the Blind River district in Canada and the Witwatersrand bankets."

CHILTON E. PROUTY, Chairman of the Dept. of Geology of the University of Pittsburgh will become head of the Dept. of Geology at Michigan State University Sept. 1. He succeeds Dr. Stanard G. Bergquist, long-time head of the department who died in March 1956.

The A.A.P.G. announces the following slate of officer nominations submitted by the nominating committee: for president, GEORGE S. BUCHANAN, Husky Oil Company, Cody, Wyoming, and SHERIDAN W. THOMPSON, Magnolia Petroleum Company, Dallas, Texas; for vice-president, GORDON I. ATWATER, consultant, New Orleans, Louisiana, and CLAUDE N. VALERIUS, consultant, Shreveport, Louisiana; for secretary-treasurer, KENNETH COTTINGHAM, The Ohio Fuel Gas Co., Columbus, Ohio, and HAROLD T. MORLEY, Pan American Petroleum Corp., Tulsa, Oklahoma; for editor, SHERMAN A. WENGERD, incumbent, University of New Mexico, Albuquerque.

EARL F. COOK has been appointed dean of the University of Idaho, College of Mines, and Director of the Idaho Bureau of Mines and Geology. Dr. Cook has been serving in an acting capacity in both positions for the past year, since the resignation of Dean J. D. Forrester.

National Science Foundation publications are available to all scientists who have need for them. Lists of publications are available from the Foundation. Requests should be addressed to the Publication Office, National Science Foundation, Washington 25, D. C.

HARRY E. LEGRAND, ground-water geologist with the Ground Water Branch, U. S. Geological Survey for the past 11 years, has opened a consulting office in Raleigh, North Carolina. His work will include ground water and related geological problems.

The Chromite reserves of the United States have been reappraised by the Geological Survey and much larger reserves and potential resources are indicated than have been published previously. The total measured, indicated, and inferred reserves in known deposits are estimated at about 3.5 million long tons of chromium oxide (Cr_2O_3) in the ground, compared with the estimated 2 million tons in 1945. This larger estimate is mostly made up of very low-grade materials that can not be mined profitably at current prices nor beneficiated by commercial methods to meet metallurgical chromite specifications.

FRANK PRESS has been appointed Director of the Seismological Laboratory of the California Institute of Technology. In assuming his new duties in July he succeeded DR. BENO GUTENBERG, who is retiring to half-time status after 27 years at Caltech and 10 years as director of the laboratory.

RICHARD M. FOOSE has been appointed to head the newly formed Earth Sciences Department of Stanford Research Institute's Physical Science Division. Dr. Foose has arrived at the Institute in Menlo Park to take over his new duties. The Earth Sciences Department will emphasize projects in the areas of geology and mineral resource development. In its initial phases, it will undertake investigations into the fields of water resources, mineral deposits, mineral economics and the geochemical processes involved in the formation of various minerals. Dr. Foose comes to S.R.I. from Franklin and Marshall College where he was chairman of the Geology Department. He has also served as a senior geologist with the Pennsylvania Geological Survey, the Pennsylvania Turnpike Commission, and as a consulting geologist.

JOHN W. SVANHOLM has accepted a contract renewal for another 2-year term as consulting economic geologist for the government of Burma.

ALLEN F. AGNEW has been named state geologist and director of the South Dakota Geological Survey to replace Dr. E. P. ROTHROCK who resigned to enter private practice.

RALPH J. BERNHAGEN is the new state geologist for the Ohio Division of Geological Survey of the Department of Natural Resources. He replaces J. H. MELVIN who is now with the Pennsylvania Drilling Company in Pittsburgh.

B. B. BROCK, consulting geologist to Anglo American Corp. of South Africa, Ltd., has been elected president of the Geological Society of South Africa.

V. A. GORSKY has joined the staff of the Geological Survey in Pretoria, South Africa. Formerly he was with the Geology Department, University of Natal, Durban.

EARL M. IRVING has been named manager of exploration activities in Brazil for the Hanna Coal & Ore Corp., Headquarters of Mineracao Hanno do Brasil, Ltda. are in Sao Paulo.

DEAN F. FRACHE, chief geologist for Union Carbide and Carbon Corp. of New York, recently visited the mines of Northern Luzon Mining and Industrial Co. in the Philippines.

E. I. TOLSTIKOV of Soviet Russia will speak to a world gathering of scientists this September at the International Union of Geodesy and Geophysics. His subject will be "Arctic and Antarctic Investigations of the International Geophysical Year."

FREDERICK C. KRUGER has been named chief geologist, Mining and Exploration Dept., International Minerals and Chemical Corp., Chicago. Dr. Kruger, formerly assistant chief geologist for Reynolds Metal Co., Little Rock, Ark., has taught geology at Dartmouth College, and was professor of geology and economic geology at the University of Tennessee.

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PLEASE TAKE NOTICE

For "BOOKS IN GEOLOGICAL SCIENCES"—a list of current and standard books on geology and related fields—available for purchase thru Economic Geology Business Office, 105 Natural Resources Bldg., Urbana, Illinois, see back pages of the No. 1, or February, 1957 issue and No. 5, or August, 1957 issue.

TABLES FOR MICROSCOPIC AND X-RAY IDENTIFICATION OF ORE MINERALS

By Alexander Novitzky

In Spanish. Pp. 270, 32 x 24 cm., linotype composition, paper bound. Price $12.

For orders: Economic Geology.

FIFTIETH ANNIVERSARY VOLUME

ECONOMIC GEOLOGY

1905–1955

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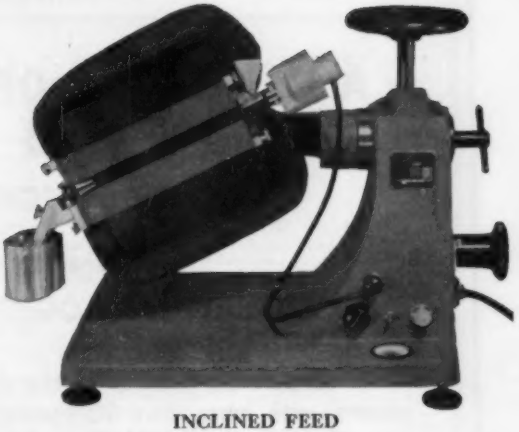

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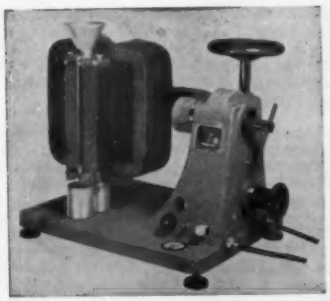

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